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INTERMEDIATE
INORGANIC CHEMISTRY

VOLUME I.

NON-METALS

BY

G. H. BAILEY, D.Sc., Lond., Ph.D. Heidelberg

LATE LECTURER IN CHEMISTRY AT THE VICTORIA UNIVERSITY OF MANCHESTER

AND

D. R. SNELLGROVE, Ph.D., M.Sc. Lond., F.C.S., A.I.C.

JOINT AUTHOR OF "QUALITATIVE INORGANIC ANALYSIS," AND
"INORGANIC CHEMISTRY, MAINLY METALS"

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PREFACE.

THIS book and *Inorganic Chemistry: Mainly Metals* have been written primarily to meet the requirements of students pursuing a course of study for an Intermediate University Examination or for examinations of similar standard.

The book is based upon *Tutorial Chemistry, Part I., Non-Metals*, by Dr. G. H. Bailey, edited by Dr. William Briggs, and the distinctive features and methods of treatment which have made that book so successful for many years have been retained, but the whole has been thoroughly revised and much has been rewritten and added in the light of modern research and experience to bring the whole up to date.

An attempt has been made to make the subject a "live" one. The historical side has been traced and the reader is given an idea of the difficulties, the errors, and the triumphs of some of the great Chemists of the past. The recognition of the value of Chemistry in manufacture and industry has made great strides in recent years, and, accordingly, the connection between the theory and the practical applications of Chemistry has been shown as clearly and as fully as a book of Intermediate standard would permit.

Over 130 experiments are included, which have been chosen so that they are easily performed and at the same time afford material assistance in grasping the context.

A chapter is wholly devoted to chemical calculations and contains miscellaneous worked examples of many types. A Table of International Atomic Weights is included as Appendix III.

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INTERMEDIATE INORGANIC CHEMISTRY, NON-METALS.

SECTION I.—GENERAL THEORY.

CHAPTER I.

HISTORICAL.

1. Introduction.—It is very difficult to say when the study of Chemistry actually started. Undoubtedly the early history of Chemistry reads more like fiction than fact, because stories of the old alchemists are full of romance and have a compelling charm. Probably the beginnings of the subject can be associated with the study of the "sacred art" by the Egyptians. Their temples were connected with laboratories in which chemical processes and operations of many types were conducted.

The actual origin of the word Chemistry is not known. Alexander of Aphrodisia used the word **chymike** to describe the operations of the laboratory, from which probably the word *chemics* was derived, and which was adopted generally a few centuries later. It is of considerable interest to know that the old name for Egypt was Cham or Chêmi (meaning "black"), and it certainly was flattering to chemists to call their art, the art of ancient Chêmi. We know for certain that the word "chemistry" was used by the Emperor Diocletian (A.D. 300), because he stated with pride that he had caused to be burnt all the Egyptian books which dealt with the chemistry of gold and silver.

2. Chinese and Egyptian Civilisations.—To the ancient civilisation of China a great deal of chemical knowledge was known; even as far back as 2000-3000 B.C. their reproductions of nature on linen, bronze, copper, and silk show that they could prepare these substances. The smelting of minerals and of bronze was known about 1800 B.C., and a long time before the Christian era the Chinese had prepared paper, gunpowder, glass, porcelain, earthenware, and varnishes.

After the Chinese the oldest civilisation is the Egyptian, and we know that the Egyptians understood the preparation of various metals and alloys, they were acquainted with glass-making, dyeing, soap-making, embalming, and with the manufacture of pigments and poisons. Alexandria was the seat of scientific activity, and here also a library of 700,000 volumes was collected, which was unfortunately destroyed in 641 A.D. *These ancient chemists were concerned mainly with the practical aspect of the subject.*

3. Greek Civilisation.—In the Grecian era which followed the Egyptian civilisation, we can trace the beginnings of theoretical chemistry. The Greeks did very little practical work, but philosophised and made speculations, although some of their rudimentary conceptions have since been shown to have a real basis of truth in the light of modern knowledge. We will briefly mention here a few Greek philosophers and their ideas.

Thales (600 B.C.), a contemporary of Solon, considered the universe to be derived from one single substance—water; Anaximenes (550 B.C.) held that air was the primordial substance, whilst Heraclitus (500 B.C.) postulated that fire was the essence and origin of all matter; Anaxagoras (500 B.C.) believed, however, in a vital substance which could be infinitely divided, but was not in motion except by the force of some immaterial, supernatural intelligence. Leucippus (430 B.C.) was fairly near the truth when he described "atoms." He said the universe is infinite, and the solid part of it is composed of very small particles, which varied from substance to substance. These small particles, or atoms, are in motion, and sometimes collide with other

atoms, and occasionally unite with similar atoms. Democritus (400 B.C.), held the same views, and said that atoms have continual motion and are eternal. These ideas of Leucippus and Democritus were handed on by Epicurus (350 B.C.), and Lucretius (90 B.C.), but another theory was propounded about the same time.

Empedocles (470-430 B.C.) was a native of Sicily, and had lived and studied in Greece. He agreed with the atomistic theory, and asserted that there were four fundamental elements—water, air, fire, and earth. This was a theory that was also held by very early Indian philosophers. Aristotle (384-322 B.C.), who was a pupil of Plato, accepted the four elements of Empedocles, and deduced four essences of nature—heat, cold, humidity, and dryness. Thus, he said water was composed of cold and humidity, and earth of cold and dryness, etc. To these four essences he added a fifth (*quinta essenza*), of a spiritual ethereal character. Aristotle was, however, a practical worker, for to find if air had weight, he weighed a bladder full of air, then weighed it deflated, and finding no difference in weight he concluded air had no weight! He studied the properties of air and concluded that "Nature abhors a vacuum," an idea that was generally believed until the time of Galileo. From Archimedes (280 B.C.), who measured specific gravity, to Pliny (23 A.D.), and for centuries after, the ideas of Aristotle were supreme.

These Greek theories of the structure and transformation of matter made the transmutation of metals appear to be possible. Most probably the deposition of copper on iron placed in a solution of blue vitriol ($CuSO_4$), was considered to be an actual case of transmutation. Gold was very valuable, and thus the problem of converting the "baser" metals, such as lead, into gold, became the main object of chemists.

4. Alchemy.—The Arabs, who were all powerful in Northern Africa in the seventh century A.D., gave the world at least one great chemist, Geber, who lived about 800 A.D. Geber tried to prepare gold, wrote many books, and described nitric acid for the first time. He was conversant with many compounds,

and chemical processes, and although a believer in Aristotle he postulated a new theory, namely, that all the metals were composed of the two substances, mercury and silver, and by varying the proportions of each it should be possible to pass from one metal to another.

The Arabs changed the word "chimica" to alchimia (alchemy) by the addition of the prefix "al," which is the Arabic word for "the." Through Spain, which was a part of the Muslim Empire, the study of Alchemy was introduced into Europe, and spread fairly soon all over the continent. Thus Albertus Magnus (1193-1282), and Roger Bacon (1214-1294), were followers of Geber, and aimed at transmutation.

5. Iatrochemistry.—With Basil Valentine (ca 1400), we come to a new period in the history of alchemy, Iatrochemistry, or the chemistry of medicines. Basil Valentine was a German monk, and though he still experimented in transmutation, his main purpose was medical, for he hoped to find a substance that would cure all diseases (*elixir vitæ*), also sometimes called "the Philosophers' Stone." Most of Valentine's writings are concerned with antimony, but mention is made of sulphuric acid, nitric acid, aqua regia, and many other substances. Valentine appears to have been obsessed with the importance of antimony and its compounds.

Paracelsus (1493-1541), was a Swiss who considered the aims of chemists should be to prepare medicines. He believed that man was a chemical combination, and that illness was the result of altering this combination, and could therefore be cured by chemical means. Paracelsus was the first to prepare hydrogen, although its true nature remained unknown till the time of Cavendish, 1766. Van Helmont (1577-1644), who followed Paracelsus, is chiefly remembered for the discovery of the existence of different kinds of gases, which had been generally grouped under the one name "air."

With the coming of Glauber (1603-1668), we arrive at the end of the period in which chemistry was the handmaid of medicine, and also the beginning of the decline of alchemy. Glauber, who discovered "Glauber's Salt" ($Na_2SO_4.10\,H_2O$)

and ammonium nitrate, etc., was a truly scientific worker, and had a fertile mind; with him Mysticism can be said to have definitely started to decline.

Lemery (1645-1717) is chiefly remembered for his popular book, *Cours de Chimie*, published in 1675, in which he divided substances into two classes, organic (animals and vegetables), and inorganic (minerals).

6. Pneumatic Chemistry.—Robert Boyle (1627-1691) is sometimes called "the father of modern chemistry." About his time alchemy and iatrochemistry were fast losing ground, and Boyle, who was a thoroughly practical scientist of the first rank, was careful to explain that chemistry should no longer be either alchemistic or medical, but should be a separate study. In his book, *The Sceptical Chymist* (1661), he outlined his ideas. Thus the old theory of the constitution of matter due to Empedocles, which said that there were only four "elements," namely, Air, Fire, Earth, and Water, was regarded by Boyle as inaccurate. He defined an element as a substance which cannot be split up into other substances; which was a tremendous advance in scientific theory. Boyle also revived the "atomistic theory" of Leucippus, and suggested that matter is composed of very small particles of different shapes and sizes; and that in chemical changes these atoms combined and separated.

Boyle, among many other discoveries, found that combustion would not take place in a vacuum, whereas gunpowder took fire in a vacuum if heated. He therefore concluded that the substance which supports combustion in air is analogous to that contained in the nitre which was one of the constituents of gunpowder. He also demonstrated that metals increased in weight on heating. It can readily be seen that Boyle was a clear thinker, a keen observer, and an unprejudiced investigator. There is no doubt that he was far in advance of his age, but unfortunately his ideas did not have the immediate effect that they deserved.

Boyle ushered in a new period of chemistry, namely Pneumatic Chemistry, which dealt with the study of gases. He perfected the air pump and discovered "Boyle's Law." The

"Royal Society" was founded by Boyle in London in the reign of Charles II.

Robert Hooke (1635-1702) was a pupil of Boyle, but did not share his teacher's view that fire consisted of small ponderable particles; also he believed that in combustion a part of the air entered into combination with what he calls the "sulphureous" body.

John Mayow (1645-1679) was the first to collect gases over water by means of the pneumatic trough. He studied combustion, double decomposition, and chemical affinity. In one experiment he burned a candle under a bell-glass over water, and observed that the volume of air diminished, leaving a gas lighter than air which did not support combustion.

Up to this time experimental work was not conducted on a quantitative basis, and weight was not yet considered to be an all important factor. "The Law of Conservation of Matter" was not generally recognised or accepted until Dr. Joseph Black (1728-1799) made it the basis of all his investigations. He discovered carbon dioxide, which he called "fixed air," explained "mild" and "caustic" alkalies (see Vol. II.), and also discovered latent heat. Priestley (1733-1804) discovered nitrogen, carbon monoxide, nitric and nitrous oxides, and oxygen. Cavendish (1731-1810) discovered hydrogen, and showed the composition of water. He demonstrated that air is a simple mixture of oxygen and nitrogen in fixed proportions, and all his experiments were quantitative. Scheele (1742-1786) discovered oxygen independently, nitrogen, chlorine, and many organic compounds. Bergmann (1735-1784) was one of the pioneers of analytical chemistry.

7. The Phlogiston Period.—The investigation of combustion was the main occupation of chemists from the time of Robert Boyle to Lavoisier (1777). The Phlogiston Theory is fully treated in Chapter XII., so we need not discuss it in detail here. Although incorrect, this theory served a useful purpose, for it was the direct cause of a great deal of work and discussion, and the discovery of many new substances. Black attacked the phlogiston theory, which was finally routed by Lavoisier (§ 92).

8. Lavoisierian Period.—With Lavoisier (1743-1794) we start the study of the modern side of the subject. The history of chemistry during the Lavoisierian Period cannot be given here in detail, but the chief points may be summarised as follows :—

(*a*) Lavoisier explained the process of oxidation and combustion.

(*b*) Richter and Fischer conducted quantitative experiments in the neutralisation of acids with alkalies.

(*c*) John Dalton put forward the "Atomic Theory."

(*d*) Gay Lussac in 1805 discovered the law of gaseous combination, which bears his name.

(*e*) Avogadro in 1811 propounded his hypothesis, and explained the relationship between vapour density and molecular weights.

(*f*) Mitscherlich in 1819 explained isomorphism.

(*g*) The Law of Dulong and Petit concerning specific heats was discovered in 1819.

(*h*) The "Law of Constant Proportions," the "Indestructibility of Matter," and the use of the balance were tacitly accepted.

We cannot easily estimate the debt that we owe to Lavoisier. He did not discover any new bodies, or new properties, but he explained the facts established by others. He put chemistry on a new basis by infusing into the whole body of science a new spirit. Lavoisier wrote a book called *Traité Elementaire de Chimie*, in which he incorporated his ideas, but in the list of thirty-three simple substances (elements) tabulated in this book, he includes heat or caloric and light as two elements !

The Atomic Theory.—John Dalton (1766-1844) made one of the greatest steps in the history of chemistry when he propounded the Atomic Theory. Dalton's theory, which is fully described in Chapter III., had little experimental evidence to support it, but it was sound. Although for some years after its inception the atom and the molecule were not completely understood, yet the atomic theory was the vital factor which enabled chemistry to be put upon the secure ground

on which it now stands. The history of chemistry since Dalton's time cannot be given in detail in this book.

9. Modern Chemistry.—From about 1800 the progress of Chemistry has been rapid. Among the vast amount of work done it is difficult to choose here and there and say certain investigations were outstanding.

Sir Humphrey Davy, the discoverer of the alkali metals, and Faraday laid the foundation stone of electro-chemistry; Berzelius, Arrhenius, Ostwald, Nernst, and many others developed it. Dumas did some brilliant work on vapour density and atomic weights. Berzelius adopted the system of representation of the various elements which we now use. The synthesis of urea by Wöhler in 1828 overthrew the belief that a vital force was necessary to prepare organic compounds. Frankland initiated and developed the idea of valency. The Periodic Law was first definitely stated by Mendeléeff. The atomic weights of many elements was determined with great accuracy by Stas. In the field of organic chemistry Liebig, Kekulé, Emil Fischer, Pasteur, Van't Hoff, Gerhardt, Laurent, and many others have done wonderful work.

To come to recent times we could mention the work of Rutherford, J. J. Thomson, Bohr, and Lewis on the atom; Mme. Curie's discovery of radium, and Soddy's development of radioactivity; Bragg's discoveries of crystal structure; Aston's work on isotopes, and the tremendous development of synthetical organic chemistry.

CHAPTER II.

PHYSICAL AND CHEMICAL CHANGES.

10. The Method of Scientific Inquiry. — Let a person unacquainted with the aims and the conduct of scientific inquiry examine some material object, say, a mineral, a piece of rock, or a pebble from the sea-shore, and let him then detail the points of interest which occur to him as the result of his examination. He may be struck by its form, its colour, its hardness, the nature of its surface, or he may be disposed to ask whence it came and how.

In what respects do his questionings differ from those of one trained in the methods of scientific investigation? In this, that the scientist is accustomed to grouping his observations, he is trained by experience to the recognition of likenesses and unlikenesses in such bodies so as to reject the trivial details, and hold firmly to the essential and characteristic ones.

Investigation by a process of comparison and classification, however, opens up such a wide field, that it becomes necessary to proceed step by step, and press the inquiry along well-defined lines, each with a distinct purpose.

The geologist, desirous of determining the history of the strata, will devote himself to the observation of existing strata, their essential and prevailing characters, their origin and mode of formation. The biologist, on the other hand, studies the structure of living organisms, classifying them according to their forms and functions, and tracing historically the occurrence and evolution of the different types. The physicist interests himself with the phenomena associated with matter, whilst the chemist deals with matter itself and its identification.

Now to all these, such objects as we have mentioned in the opening paragraph will appeal in a variety of ways. A piece of chalk, limestone, or marble are very different objects to the geologist, but may be much the same thing to the chemist if he finds them to be composed of the same kind of matter. A piece of glass rubbed briskly with silk becomes capable of attracting small light bodies ; this observation is of little direct importance to the chemist if he finds that the substance of the glass has not changed or its mass become greater, though to the physicist such an observation may be of great significance. A piece of iron, so far as the chemist is concerned, retains its identity as iron whether it be in the form of a solid bar, the finest wire, or an impalpable powder ; it may grow warmer and expand, or by cooling contract ; it may be endowed with the property of attracting other particles of iron or not, and yet its composition and mass may remain unchanged. So long as any modification of aspect or behaviour is such as experience has taught him belong to matter which he identifies as *iron* he maintains that no alteration in substance has taken place.

To sum up, we may say that the method of scientific inquiry as applied to Chemistry consists in experiment, observation, and inference.

11. Transmutation of Metals.—The earlier chemists believed that they could change the baser metals into noble metals, quicksilver into gold or lead into silver, and most of their researches were pursued with this object in view. The more searching methods of inquiry adopted in later times have, however, shown that their conclusions were fallacious.

So also, even in the time of Lavoisier, towards the close of the eighteenth century, chemists failed to realise what takes place when iron rusts or metals burn, although an actual change of substance has taken place, and matter is indeed added to the metals during the process.

These misunderstandings arose from two main sources :

(1) Failure to appreciate the *essential and characteristic* properties of the substance under consideration.

(2) Failure to test whether any *apparent* alteration of

substance had been accompanied by increment or loss of substance during the experiment.

At each step the balance must be called upon to say whether any increment or loss of substance has taken place, and if so the source of this change in mass must be traced.

All conclusions, and especially those which form the foundation of further investigation, require to be fully and critically examined in order to see that the deductions drawn are justified by the facts.

12. The Field of Inquiry for the Chemist.—The aim of the chemist is then to investigate matter with a view to recognising and classifying the *essential* characters of each kind of matter, and to follow the changes which ensue whenever those changes involve a redistribution of matter.*

Let us then follow the course of investigation by experiment, which will enable us to see how the information we require is to be obtained, and what deductions may be fairly made from the observations.

Exp. 1.—An Apparent Transmutation of Iron into Copper.—Into a solution of "blue vitriol" dip the bright blade of a penknife. After a short time remove the knife. Observe that the part of the blade which was immersed in the liquid has acquired the appearance of copper.

Apparently the iron of which the blade is composed has been changed into copper, and if you were to leave the investigation at this stage you might conclude that you had succeeded in bringing about a transmutation of iron into copper. It is only after you have carried out an exhaustive inquiry, and performed a series of somewhat complex experiments that you will be in a position to decide what is the nature of the change you have observed.

13. The Nature of Physical and Chemical Change.—At the outset of any inquiry relating to the science of chemistry it is necessary to acquire clear ideas as to the nature of chemical

* Whether in the operations which he performs matter may be created or destroyed must for the present remain untouched. An appeal to his later observations must decide this.

change and the distinction between this and physical change, and in such an inquiry the use of the balance is indispensable.

Exp. 2.—Take the following objects :—

1. A short length of glass rod.
2. A porcelain crucible.
3. A few inches of platinum wire fixed in a glass rod.

Weigh each of these carefully (seeing that they are quite dry and clean). Now heat them for some minutes in the non-luminous flame of a Bunsen burner; observe the alterations which ensue during the heating, *e.g.*, change of colour, softening. In heating a crucible it will be desirable to support it on a pipe-clay triangle as shown in Fig. 1.

Allow the objects to cool, and see how far they resume their original character. Weigh them when quite cold, and compare with your first weights.

Exp. 3.—Now perform similar experiments with the following bodies, and make observations upon them in the same way :—

4. A fragment of sulphur in a test-tube.
5. A fragment of wax in a test-tube.
6. A few crystals of iodine in a test-tube.

Carefully observe and note down any changes during the application of the heat, and also what takes place during the period of cooling. A pocket lens will be of assistance to you in some of your observations.

Do not press the heating so strongly as to drive vapours out of the mouth of the tube. (Find out, however, in the last example how it would affect the records you have made if you do so drive off vapours.)

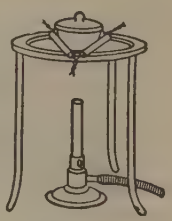

Fig. 1.

Exp. 4.—Heat for at least fifteen minutes in small porcelain crucibles, and record your observations as before :—

7. Some small pieces of magnesium foil (with crucible cover loosely on).
8. Some small pieces of tin (without cover).
9. ,, ,, wood (without cover).

Having now before you the records of all your observations arranged in an orderly manner, you may collect them, *i.e.* generalise them, under the following heads :—

(*a*) Those cases (1-6) in which there is no substantial*

* It will be useful to consider how very small variations having no particular bearing on the inquiry may occur, and how precautions might be taken to eliminate them.

alteration of weight, and in which, though whilst the heat was being applied changes of colour, etc., may have been evident, yet on cooling, the substance had, so far as we can judge, returned to its original form and character.

While hot the glass rod softened, became out of shape, and gradually acquired a red colour, the porcelain crucible became red-hot, and the platinum wire white-hot, and softer so that it could be more easily drawn asunder; but all three objects regained their original appearance and properties on cooling, though the test-tube remained out of shape.

Again the sulphur and wax melted on heating but solidified on cooling, and then exactly resembled other fragments of the original substances; the iodine volatilised without melting, forming violet vapours, but when the test-tube was allowed to cool these vapours condensed on the sides of the tube in the form of blue-black crystals exactly like those originally taken.*

(*b*) Those cases (7-9) in which alteration of weight (gain or loss) has taken place, and in which it will be observed that a distinct change in character and properties has been brought about.

Thus the magnesium was converted into a very light fluffy white powder and the tin into a white powder, in both cases with gain in weight, whilst the wood gradually burned away with loss of weight. Thus in each case a new substance was formed.

We recognise a striking difference in behaviour under the action of heat. Thus we find that substances often gain in weight under the action of heat, and it was this which led the earlier inquirers to the conclusion that heat was a ponderable substance, and that the increase in weight was due to the addition of matter, which they called "caloric," to the body which was exposed to it.

For the present, however, let us confine our attention to the cases under Exps. 2 and 3, in which no alteration of weight has been found to take place and no permanent alteration of properties.

* This phenomenon (of volatilising without melting) exhibited by iodine on heating is called *sublimation*.

Many familiar examples of this class of phenomena will readily occur to you. Water is well known by its appearance and character, and is presented to us commonly as rain, or collected in rivers and in the sea. In the depth of winter, however, we see it become transformed into solid ice or snow, and later changing once more into water. The inhabitant of the Arctic regions is more familiar with it as ice, and the liquid water is to him a rarity. In tropical regions the reverse is the case, ice or snow being seldom seen. Yet we can readily satisfy ourselves with the aid of the balance, that ice passes into water or water into ice without change in weight or substance. And, similarly, we may examine the relation between steam or water vapour and water itself.

In the solid form it is ice or snow, in the liquid form it is water, in the gaseous form it is steam or vapour, and all forms consist of hydrogen and oxygen in the proportion of two volumes of hydrogen to one volume of oxygen. The matter is the same, the form of its occurrence is different. That matter may exist in solid, liquid, or gaseous forms and yet be in substance the same is not the exception but the rule. The difference of character is a difference of *physical state.*

Whether the substance is present to us as ice, or water, or vapour, depends on the *physical conditions* which prevail, and we realise by ordinary experience that *temperature* is the controlling factor. Yet ice may be transformed into water by *pressure* alone, or by sprinking it with common salt.

Summarising the results which these and similar observations bring home to us we find—

(1) That matter may change in form (expand or contract), it may change in state (gaseous, liquid, solid), it may change in character (an impalpable powder, a crystalline solid), or it may become softer or more brittle, porous or more dense, without any alteration of mass or variation of substance. Such temporary modifications of character are classed as *physical changes.*

(2) That matter may undergo modifications in the properties which it exhibits in response to the communication from without of heat, light, electricity, which are capable of being

stored up by it, but which are imponderable, and therefore likewise bring about no alteration of mass. Such properties are termed *physical properties*.

On the other hand the permanent modifications of character which matter undergoes when its mass is altered (as in Exp. 4) are classed as *chemical changes*, and those properties of matter which it exhibits when it undergoes chemical change are termed *chemical properties*. We may define these two changes as follows :—

A physical change is a change which involves an alteration in the properties of a substance or substances, but does not involve the formation of a new substance or substances.

A chemical change is a change which involves the formation of a fresh substance, or substances, with different properties from the original substance or substances.

14. Mixtures and Compounds.—We may bring together sand and sugar, or common salt and soot, etc., *in any proportions we please*, and the first *mixture* will be the sweeter, and will dissolve in water the more freely the greater the proportion of the sugar is ; the latter, with a predominance of soot, will be very dark in colour, and with a predominance of salt may be only faintly grey. An infinitely large number of mixtures could be made, all slightly differing in taste and appearance, and also in respect of the extent to which the mixture will dissolve in water. In any of the mixtures you might, however, by very simple means recognise the sand and the sugar, or the soot and the salt, and it is also an easy matter to separate them, *e.g.* by shaking up with water and filtering, when the sugar or salt dissolves and passes through the filter, whilst the sand or soot remains on the filter.

Exp. 5.—Mix together intimately seven parts by weight of finely-powdered iron and four parts of flowers of sulphur. Heat one-half of the mixture over a Bunsen burner in a small porcelain crucible for a few minutes with the lid on. Allow to cool, and powder some of the product very finely. Compare with the rest of the mixture : you will notice a difference in colour. Draw a magnet through each of the powders. You will find that iron is extracted from the mixture which has not been heated, and a residue of sulphur remains. No iron can, however,

be extracted by means of a magnet from the substance formed on heating; a *chemical compound* has been formed. Shake up a little of each of the powders with carbon disulphide. Filter. Allow the filtrate to evaporate. In the case of the mixture a residue of sulphur remains, but there is no appreciable residue* in the case of the compound.

Drop a little of each of the powders into some dilute sulphuric acid contained in separate test-tubes. Note that in the case of the mixture hydrogen is evolved and a residue of sulphur remains, whilst in the case of the compound an evil-smelling gas (sulphuretted hydrogen) is evolved, and no residue* remains.

In the **mixture** of iron and sulphur, then, the two elements retain their individual properties, iron its magnetic properties and its solubility in dilute acid with evolution of hydrogen, sulphur its solubility in carbon disulphide, and insolubility in acid; in the **chemical compound,** on the other hand, these individual properties of the two elements are completely lost. The constituents of the mixture can readily be separated by making use of their individual properties, but the constituents of the compound cannot be separated in this way.

Similar experiments with other substances lead to similar results, and we may define a *chemical compound* as *a substance produced by the union of two or more simpler substances in such a way that the individual properties of the constituents have disappeared.*

QUESTIONS.—CHAPTER II.

1. Briefly explain what you understand to be the *method of scientific inquiry.*

2. To what chief causes were the mistakes of the early chemists due?

3. What do you consider to be the field of inquiry for the chemist?

4. Describe an experiment illustrating the apparent transmutation of one metal in to another.

5. Explain the difference between a *physical* and a *chemical* change, giving examples.

6. What are the characteristics of mixtures and compounds?

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* There may be a slight residue of sulphur owing to the incomplete combination of the iron and sulphur.

CHAPTER III.

THE ATOMIC THEORY AND THE LAWS OF CHEMICAL COMBINATION.

15. The Atomic Theory.—We have seen in Chapter I. that the Greek philosophers, notably Leucippus, formulated the **atomic theory**; its progress up to the time of John Dalton (1766-1844) is also traced. But the ideas of Leucippus and those who accepted them, were necessarily speculative, and were not tested experimentally. Dalton, however, gave the Atomic Theory to the world after considerable thought, and it was a theory capable of explaining many of the facts then known. Further, it was most certainly capable of being tested. As previously stated (§ 9) Dalton did not propound the Atomic Theory after a consideration of experimental results. His method consisted in thinking out the theory and then conducting experiments to test its truth.

Dalton's Atomic Theory may be summarised as follows :—

(1) Matter is composed of atoms.

(2) Atoms of the same element are identical in size and weight, and different from those of other elements.

(3) Atoms cannot be created or destroyed.

(4) Compounds are formed by the combination of atoms in *simple* integral ratios.

(5) "Compound Atoms" (molecules) are formed by the union of two or more elementary atoms.

It is a great tribute to Dalton that it is only in the light of discoveries of very recent years that any of these statements need modification. The discoveries of isotopes and radioactivity (See *Inorganic Chemistry, Mainly Metals*) call for a slight revision of numbers (2) and (3) respectively.

16. Explanations by the Atomic Theory.—Dalton's Atomic Theory explained the laws of chemical combination, and from it the following laws can be directly deduced.

(*a*) The Law of the Conservation of Matter.

(*b*) The Law of Fixed Proportions.

(*c*) The Law of Multiple Proportions.

(*d*) The Law of Reciprocal Proportions.

We shall now proceed to discuss these laws in detail.

17. The Law of the Conservation of Matter. History.—Although the principle of the indestructibility of matter was assumed by many investigators, the law was first definitely stated by Lomonossoff in 1756. Joseph Black, in his researches, accepted it. Lavoisier also tacitly assumed it and explained his theories, using it as a basis. Since then various workers have tested its validity, but in every test it has been shown to be true.

We may define the **Law of Conservation of Matter** as follows :—**In the course of chemical operations matter is neither destroyed nor created.** The following experiments can be performed by the student to illustrate the law.

Exp. 6. (*a*) Take a clean, dry litre flask, and fit it with a good cork. Cut off from a stick of ordinary phosphorus a piece of about the size of a pea, taking care to perform this operation under water. Dry the piece of phosphorus with filter paper, place it in the flask, fit in the cork, and weigh the whole. Now ignite the phosphorus by dipping the flask into hot water. The flask will soon be filled with white fumes of oxide of phosphorus. When the flask is cool, wipe it dry and weigh again. The weight will be found to be the same as before.

(*b*) Take two small beakers. Pour into one a little copper sulphate solution and into the other a little caustic potash solution. Weigh the two beakers together. Now pour the caustic potash into the copper sulphate, taking care not to lose any liquid. Double decomposition takes place, and a bulky precipitate of copper hydroxide is formed. Weigh the two beakers again together. The weight is the same as before.

It is clear that in these two experiments there has been no creation or destruction of matter but merely a redistribution,

18. The Law of Fixed or Constant Proportions.—Towards the end of the eighteenth century chemists accepted the Law of Constant Proportions. J. L. Proust was really the first to enunciate the law, and he had a controversy lasting eight years (1800-8) with Berthellot on its validity. Here are Proust's own words: "According to my view, a compound is a privileged product to which nature has assigned a fixed proportion. . . . Between pole and pole compounds are identical in composition . . . in all the world there is but one sodium chloride, one saltpetre. . . ."

We may define the Law of Constant Proportion as follows :—

The same compound always contains the same elements in the same fixed proportion by weight. The student can test this law by experiment.

Exp. 7. Composition of Oxide of Magnesium.—Weigh a clean, dry porcelain crucible with its lid. Measure off 12 cm. of *bright* magnesium ribbon (scrape the ribbon with a knife if it is not bright), roll it up *loosely* and place in the crucible ; then weigh the whole. Fix it securely on a pipe-clay triangle and tripod. Heat the closed crucible sufficiently to cause the metal to burn when the lid is slightly raised. Do not let any white fumes escape. When the burning has nearly ceased remove the lid, but continue to heat for a few minutes longer. Cool and weigh the whole again. Heat till the weight is constant, showing that the change is complete. Tabulate your results like this—

	grammes.
Weight of crucible, lid, and magnesium	=
,, crucible and lid	=
,, magnesium	=
,, crucible, lid, and magnesium oxide (1) ...	=
,, ,, ,, ,, ,, (2) and (3) (constant—suppose)	=
,, magnesium oxide	=
Increase in weight of metal, *i.e.* weight of oxygen ...	=

Weight of oxygen combined with one part by weight of magnesium, *i.e.*

$$\frac{\text{Weight of oxygen}}{\text{Weight of magnesium}} =$$

Now repeat the whole experiment, using a different weight of magnesium.

You will find that, however many times you perform the experiment, you will alway obtain the same result on calculating out the weight of oxygen which combines with one part by weight of magnesium.

Let us now prepare oxide of magnesium from magnesium in another way, and see whether the proportions of oxygen and magnesium are the same as before.

Exp. 8. As in Exp. 7, weigh a crucible and lid, add the magnesium to the crucible, and weigh the whole. Cover the magnesium with as little water as possible. Place in a fume cupboard and add a few c.cm. of concentrated nitric acid. Put the lid on to avoid loss by spirting, but so that the brown fumes may escape. When all action has ceased and the magnesium is dissolved, evaporate the solution to dryness carefully. With great care heat to decompose the magnesium nitrate. Cool in a desiccator and weigh. Heat till the weight is constant. Tabulate your results as before.

You will find that the result is the same as in Exp. 7, *i.e.* whether magnesium oxide is made as in Exp. 7 or in Exp. 8 its composition is the same.

Exp. 9. Composition of Chalk.—Powder some pure chalk and place it in a weighed crucible, and obtain the combined weight of crucible *plus* chalk. Now heat strongly with a blow-pipe flame for quite a long time. Allow to cool, and weigh again. It will now weigh less than before. Repeat the heating and weighing till there is no change in weight. Be careful to direct the flame against the bottom of the crucible. The total loss should be about 44 per cent. This represents the *carbon dioxide* which is driven off by heat; the residue is *quicklime*. Repeat the experiment with a different weight of chalk. You will again find that the loss in weight is 44 per cent.

Chalk, then, is composed of carbon dioxide and lime *combined in fixed proportions.*

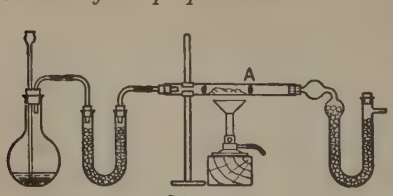


Fig. 2.

Exp. 10. Composition of Water.—Take a hard glass tube about 20 cm. long and 1·5 cm. wide, and fit it with corks. Push into the tube a loose plug of asbestos (which has been previously ignited and allowed to cool in a desiccator) so that it is about a quarter of the way up the tube (A, Fig. 2). Weigh out approximately 5 grm. of finely-powdered black oxide of copper,* and introduce it into the tube at the end remote from the

* This should be previously heated to redness in air (to get rid of moisture, etc., attached to it), and, whilst still warm, introduced into the tube just before commencing the experiment.

asbestos, by means of a small funnel. Now introduce a second plug of asbestos (ignited as before), carefully pushing it up the tube so that it sweeps along all particles of oxide. The distance between the two asbestos plugs should be about 6 cm. Place the tube horizontal and tap it so that the oxide forms an even layer with a free air space all along the tube. Carefully wipe off any oxide from the outside of the tube.

Next weigh the tube and copper oxide accurately. Also weigh a U-tube containing granular calcium chloride, and united with a horizontal bulb as shown in the diagram. Attach the U-tube and bulb to the straight tube as shown (arranging that the tube which passes through the cork *does not reach beyond it**). Connect the other end of the tube to a supply of hydrogen prepared by the action of dilute sulphuric acid on zinc, and dried by passing through a U-tube filled with granular calcium chloride. Allow the hydrogen to pass through the tube for a few minutes in order to displace the air. (Test if the air has been removed in the usual way—see page 118.)

Heat the oxide of copper by means of a flat-flame burner. The colour of the oxide of copper will slowly change to a dark red, and water will be seen to condense in the farther end of the tube and the horizontal bulb. The heating must be continued and the stream of hydrogen passed until no more traces of moisture are observed in the straight tube. You will find it necessary to warm the farther end of the tube in order to drive out the water which collects there. Do this with an ordinary Bunsen burner, taking care that the tube does not become so hot as to affect the cork. Most of the moisture will now collect in the horizontal bulb, and the rest will be absorbed by the calcium chloride.

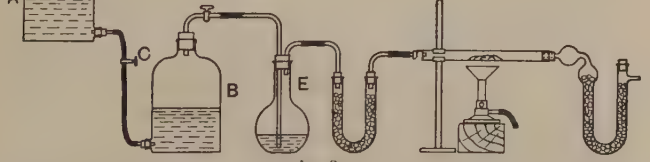


Fig. 3.

Now allow the apparatus to cool, still passing a slow current of hydrogen. When cold disconnect the hydrogen generating flask, leaving the calcium chloride tube in place. Now pass a slow current of dry air through the apparatus by means of the arrangement shown in Fig. 3.† The upper bottle A is filled with water, which flows down into B when

* If it did you would be unable subsequently to drive all the water out of the tube.

† A simpler way is to use a "*scent bottle*" *bellows*.

the tap D and screw-clip C are open, and forces the air out through the exit-tube. The air is first passed through a small sulphuric acid wash-bottle E, which serves to indicate the rate of flow and also partially dries it. It then traverses the remainder of the apparatus (being further dried by the calcium chloride in the U-tube), and sweeps out the hydrogen.* The current of air is regulated by the tap and screw-clip, and should be maintained for about five minutes.

Reweigh the tube (+ copper) and the U-tube and bulb. We have now all the data necessary for calculating the ratio of hydrogen to oxygen in water. Enter you results thus :—

	grammes.
Weight of heating tube + copper oxide	$= x$
,, ,, ,, ,, + copper	$= y$
,, oxygen which has been converted into water	$= x-y$
,, U-tube and bulb before experiment ...	$= a$
,, ,, ,, ,, after ,, ...	$= b$
,, hydrogen in the water formed	$= b-a-(x-y)$

Hence—

Weight of oxygen united with 1 grm. of hydrogen is $\frac{x-y}{b-a-(x-y)}$

You should find this to be about 8 grm. Repeat the experiment and show that you get the *same result.* Now try another oxide in place of copper oxide—say litharge ; again the result will be the same.

A very large number of experiments have been made similar to those you have just performed, and all have led to similar results, which may be generalised in the statement known as the *Law of Constant Proportion* (§ 19).

19. Law of Multiple Proportion. History.—Dalton deduced the Law of Multiple Proportion from his Atomic Theory. Being a brilliant scientist, he then investigated it experimentally, using certain compounds of carbon and hydrogen, which gave the results he anticipated.

The **Law of Multiple Proportion** may be defined as follows :— **When one element combines with another in more than one proportion the different quantities of the one element which unite with a fixed quantity of the other element bear a simple ratio to one another.** The truth of this law may be tested experimentally by the student as follows :—

* If you weigh with hydrogen in the tubes instead of air, you will introduce errors ; for the previous weighings were made with air in the tube, and hydrogen is much lighter than air.

Exp. 11. Weigh accurately into a small porcelain boat (Fig. 4) about a gramme of puce-coloured oxide of lead. Push the boat into a hard glass tube of about the same size as that used in Exp. 10. Fit the tube with corks, carrying short pieces of glass tubing. Now connect one end of the tube with an apparatus for preparing dry hydrogen. Allow the hydrogen to pass through the tube for a few minutes to displace the air (test as usual).

Heat the boat gently by means of a flat-flame burner. The powder gradually changes colour, while *steam* passes out of the tube along with the unused hydrogen. When the cloud ceases and the powder has become quite black (*i.e.* changed into metallic lead), raise the boat to red heat for a few seconds to fuse the lead, while the current of hydrogen still passes. Cool, stop the current of hydrogen, withdraw the boat by means of a copper wire from the end of the tube attached to the hydrogen apparatus (because there will probably be some drops of water at the other end) and reweigh it. Enter your results thus :—

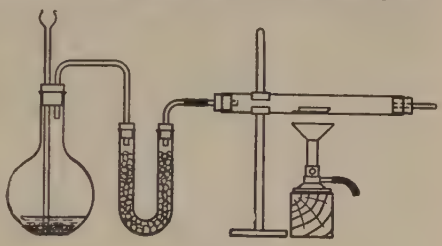


Fig. 4.

	grammes.
Weight of boat + puce oxide of lead	$= x$
,, boat	$= y$
,, boat + lead	$= a$
,, lead in oxide taken	$= a-y$
,, oxygen in oxide taken	$= x-a$

Therefore the weight of lead combined with one part by weight of oxygen in puce oxide of lead is $\frac{a-y}{x-a}$ grm.

Your result should work out at about 6·45 grm.

Now repeat the experiment, using litharge (yellow oxide of lead) instead of puce oxide of lead, and again calculate out the weight of lead which was in combination with one gramme of oxygen. The weight found should be about 12·9 grm.

Now 6·45 : 12·9 = 1 : 2, *i.e.* the weights of lead which unite with 1 grm. of oxygen to form puce oxide of lead and litharge respectively are in the ratio 2 : 1.

There is then a very simple relation between the relative weights of oxygen which combine with a fixed weight of lead to form these two oxides of lead.

Exp. 12. Clean and heat a porcelain crucible and lid, and allow them to cool. Place in the crucible about 1 grm. of well-powdered recrystallised copper sulphate crystals, and accurately weigh the whole. Heat, with the lid off, for half-an-hour in an air oven (Fig. 5) kept at a temperature of 135° C. to 140° C. Stir the powder occasionally with a platinum wire. When properly heated it should appear whitish all through. Allow the crucible to cool with its lid on, and weigh again. The difference in weight gives the weight of water lost.

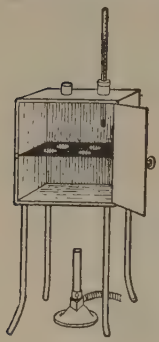


Fig. 5.

Next support the crucible on a pipeclay triangle, and heat it very carefully (without the lid), using a small flame, which is not allowed to touch the crucible. Cool with the lid on, and weigh. The heating and cooling should be repeated until practically a constant weight is obtained, when all water will have been expelled. The difference between this weight and the former shows the loss of water due to the raised temperature. It should be just one quarter of the first loss.

The results obtained by a student were as follows:—

	grammes.
Weight of crucible, lid and powdered crystals	13·727
,, crucible, lid, and powdered crystals after heating to 140° C.	13·440
,, water expelled at lower temperature	0·287
,, crucible, lid, and anhydrous copper sulphate ...	13·367
,, water expelled at higher temperature	0·073
Total weight of water in the crystals	0·360

Thus the proportion of water in the crystals to that in the first product was found to be 0·360 : 0·073, or 5 : 1, or, in other words, the weights of water which unite with a fixed weight of copper sulphate to form two different compounds bear to one another the simple ratio 5 : 1.

Similar experiments with other substances have led to similar results. Thus :—

12 grm. of carbon combine with 16 grm. of oxygen to form carbon monoxide.

12 grm. of carbon combine with 32 grm. of oxygen to form carbon dioxide.

Therefore ratio between the weights of oxygen combining with the same weight of carbon is 1 : 2.

32 grm. of sulphur combine with 32 grm. of oxygen to form sulphur dioxide.

32 grm. of sulphur combine with 48 grm. of oxygen to form sulphur trioxide.

Therefore ratio between the weights of oxygen combining with the same weight of sulphur is 2 : 3.

20. The Law of Reciprocal Proportions. History.—J. B. Richter (1762-1807) developed and tested experimentally the *Law of Reciprocal Proportions*. He used a number of acids and neutralised them with bases. Thus he compared the quantities of nitric and sulphuric acid which neutralised equal weights of potash. Previously Cavendish, in 1788, had described as *equivalent* the weights of potash and of marble which saturated the same quantity of acid. Richter, however, tabulated the weights of various bases which will neutralise 1,000 parts of sulphuric acid or a tabulated quantity of any other acid. Berzelius, realising the importance of Richter's observations, found that 100 parts of iron, 230 parts of copper, and 381 parts of lead are equivalent, for they combine with 29·6 parts of oxygen to form oxides, and with 58·73 parts of sulphur to form sulphides. Berzelius extended Richter's results to combinations between elements.

The **Law of Reciprocal Proportion,** which deals with the case in which two elements combine with a third element, may be defined as follows :—**The relative proportions in which two elements combine with a third element are in a simple ratio to those, in which they combine with one another, or with a fourth element.**

Thus take the case of sodium, chloride, and iodine. In sodium chloride, NaCl, 1 grm. of sodium unites with 1·54 grm. of chlorine ; in sodium iodide, NaI, 1 grm. of sodium unites with 5·52 grm. of iodine. Therefore, if iodine and chlorine combine together they should do so in the proportions $\frac{5{\cdot}52}{1{\cdot}54} = \frac{3{\cdot}58}{1}$, *i.e.* the ratio of the weights of these two elements in which they combine with the same weight of sodium. Now iodine and chlorine combine together to form iodine trichloride, ICl_3, in the proportion of 1·19 grm. of iodine to 1 grm. of chlorine. And $\frac{3{\cdot}58}{1} : \frac{1{\cdot}19}{1} = 3 : 1$; that is a simple ratio.

QUESTIONS.—CHAPTER III.

1. What do you understand by *Dalton's Atomic Theory?*

2. What do you understand by the *Principle of the Conservation of Matter?* Describe how you would proceed to illustrate the truth of this principle by experiment.

3. State the *Law of Constant Proportion*, and describe how you would proceed to demonstrate its truth by experiment.

4. State the *Law of Multiple Proportion.* Describe experiments which illustrate it.

5. Show that the following numbers illustrate the Law of Multiple Proportion :—Red oxide of copper contains 88·8 per cent. of copper and 11·2 per cent. of oxygen. Black oxide of copper contains 79·87 per cent. of copper and 20·13 per cent. of oxygen.

6. Show that the following numbers illustrate the Law of Constant Proportions :—2·4 grm. of oxide of iron on complete reduction by hydrogen yielded 1·68 grm. of iron ; 2·9 grm. of the oxide yielded on similar treatment 2·03 grm. of iron.

7. You are provided with a powder containing copper and sulphur in the proportions of 63 : 32. Describe how you would proceed to find out whether it is a mixture or a compound of the two elements.

8. State the Law of Reciprocal Proportions. Give an example to illustrate it.

CHAPTER IV.

CHEMICAL EQUIVALENTS: VALENCY.

21. Chemical Equivalents. History.—We have seen in the previous chapter that Cavendish, in 1766, had used the word equivalent for the weights of sulphuric acid and nitric acid which would separately neutralise a definite quantity of caustic potash or of marble. The Arab Chemist Al Jildaki is said to have written (ca 1360 A.D.) that "Substances react only by definite weights," and this principle was generally held to be true by most chemists of the time. Chemical equivalents were not determined until Richter postulated the Law of Reciprocal Proportions (§ 20). Berzelius recognised that the composition of a large number of compounds could be calculated from the results of a few careful analyses. Thus he says: "It follows from the researches of Richter, that from good analysis of a few salts, one could calculate with precision the composition of all the others." Here then we have the beginning of the importance of *combining weights*, and hence *the start of fixing definite formulae for compounds*.

Richter used 1,000 parts of sulphuric acid as a standard for comparing equivalents, but this was found to be of no use when elements were considered. Dalton chose one part of hydrogen as the standard weight in terms of which the equivalent weights of all the other elements could be expressed, and this was generally accepted until recently. Berzelius, however, used 100 parts of oxygen, and determined the equivalents of many elements. Stas (1813-1891) determined many equivalents with great accuracy, and his work is considered classical. More recently similar work has been done by Guye at Geneva, and by Richards in America.

At the present time eight parts of oxygen is used as the standard, because all the elements except fluorine, and the members of the helium group, combine directly with oxygen, whereas only comparatively few hydrides are formed. The equivalent of hydrogen is then 1·008. The **chemical equivalent** of an element may be defined as the **weight of that element which combines with eight parts by weight of oxygen.**

The student must clearly understand that the equivalent is a *number only.* Thus when we say that the chemical equivalent of silver is 53·9 we mean that 53·9 parts by weight of silver will combine with 8 parts by weight of oxygen, regardless of the system of weights we use. Further, the terms "equivalent" and "combining weight" are used synonymously with "chemical equivalent."

We give below some of the methods used for the determination of equivalents of the elements.

A. The Metals.

(1) *By Determination of the Volume of Hydrogen Evolved.*—The method consists in treating a known weight (say x grm.) of the metal with dilute acid, measuring the volume of hydrogen evolved, and calculating the weight (say y grm.) from the volume. Then the equivalent of the metal is $\frac{x}{y}$. A convenient metal to use is magnesium.

This method may be used for determining the equivalents of the metals zinc, iron, and aluminium, but in the case of the last, fairly concentrated *hydrochloric* acid must be used, as dilute sulphuric acid is without action on the metal.

(2) *By Deposition of the Metal.*—Another method by which the equivalent may be determined is applicable in some cases where the foregoing cannot be used. This is the deposition of a metal from a solution of one of its salts by placing in it another metal. For instance, if metallic zinc of iron be introduced into a solution of silver nitrate or copper sulphate, etc., finely-divided silver or copper will be thrown down, and

the amounts deposited under like conditions are proportional to the equivalents of the metals in question.

Similarly, if a solution of nitrate of silver be substituted for that of copper sulphate, the equivalent of silver may be determined. Experiments of the same kind may be performed with metallic iron and copper sulphate, and with iron or magnesium and silver nitrate.

(3) *By Conversion into the Oxide.*—In many cases the most convenient method of finding the equivalent of a metal consists in converting a weighed quantity of it into its oxide, and weighing the oxide produced. From the results obtained we calculate the weight of the metal which combines with 8 grm. of oxygen (say x grm.). Then x is the equivalent of the metal.

Sometimes, as in the case of magnesium, the metal is readily converted into its oxide by heating in air. Usually it is best first to convert the metal into the nitrate, and then break this up by ignition, when a residue of oxide remains.

(4) *By Conversion into the Chloride.*—In some cases methods 1-3 may not be suitable, and a weighed quantity of the element can be converted into the chloride. The weight of the element which combines with 35·5 grm. of chlorine, *i.e.* the equivalent, can be calculated.

(5) *By Electrolysis.*—Faraday showed that the weights of substances liberated at the electrodes on electrolysis are in the ratio of the equivalent weights. If the weight of a metal deposited, and the weight of hydrogen liberated by the same quantity of electricity are determined, the equivalent of the metal can readily be calculated.

(6) *By Conversion into another Compound.*—Thus a compound of the metal with an element of known equivalent weight is converted into a compound with other elements of known equivalent weight; *e.g.* if we wish to find the equivalent of barium and know the equivalent of chlorine and of the sulphate group, we can convert barium chloride into barium sulphate, and then calculate the equivalent of barium. Actually a known weight of barium chloride (x grm.) is converted into barium sulphate (y grm.). If E is the equivalent

of barium, 35·5 and 48 the equivalents of chlorine and the "sulphate" group respectively, then—

$$\frac{x}{y} = \frac{E + 35{\cdot}5}{E + 48},$$

from which we can calculate E.

B.—The Non-metals.

Most of the non-metals are gases, and the determination of their equivalent is therefore more difficult. The following methods are suggested :—

(1) By conversion into the hydride.

(2) By conversion into the oxide or chloride.

(3) By an application of method (6) above.

It should be noted that some elements have more than one equivalent. Thus tin forms two oxides, stannous oxide, SnO, and stannic oxide, SnO_2; the equivalents being 118·7 and 59·35 respectively. Another example is sulphur which forms sulphur dioxide, SO_2, and sulphur trioxide, SO_3.

22. Equivalent Weight of Compounds.—The equivalent weight of an acid e.g. sulphuric acid, may be defined as the number of grammes of the acid which will yield 1·008 grm. of hydrogen on treatment with zinc. Similarly if the equivalent of an acid is known then the weight in grammes of caustic potash or soda which this will neutralise is the equivalent of the base used. In volumetric analysis a *normal* solution of a substance contains the equivalent weight in grammes of the substance dissolved and made up to one litre of solution, and the student will readily see that *equal volumes of normal solutions are equivalent to one another.*

23. Valency. History.—When the atomic theory was generally accepted, the atoms were considered to have an equal capacity for combination with one another. The laws of chemical combination which followed, and the acceptance of certain fundamental "types" to which all compounds were said to belong, paved the way for the idea of valency.

Dumas showed, in 1834, that one "atom" of chlorine replaced one "atom" of hydrogen in certain compounds. Liebig, later, found that three atoms of hydrogen combine with one atom of antimony. The word "valency" came to be used to mean "replaceable value," "saturation capacity," etc., but Wurtz, Kolbe, and many others were very vague in their conceptions of the meaning of valency. Frankland (1825-1899), however, did more than any other investigator to fix a definite meaning to valency. He observed that carbon silicon, titanium, and zirconium were in general "tetravalent," and therefore grouped them together. He also found that in some compounds nitrogen, phosphorus, antimony, and arsenic were "tervalent," whereas in other compounds they were "quinquevalent," and said that the elements could exhibit variable valency. A W. Hofmann used the word "quantivalency" in 1865, and in 1868 Wichelhaus shortened the word to valency, which is now in general use.

It was not until about 1907 that valency was considered to be an electronic property, when Sir J. J. Thomson put forward the view that valency depends on the transference of electrons from atom to atom. Since then many views of valency have been put forward which are, however, too advanced to be discussed here.

A good way to study valency is to consider the composition of a number of stable compounds of hydrogen and another element. The formulae of ten such compounds are given below :—

HF,	HCl,	HBr,	HI,
Hydrofluoric acid.	Hydrochloric acid.	Hydrobromic acid.	Hydriodic acid.
	H_2O,	H_2S,	
	Water.	Sulphuretted hydrogen.	
	H_3N,	H_3P,	
	Ammonia.	Phosphoretted hydrogen.	
	H_4C,	H_4Si.	
	Marsh gas.	Silicon hydride.	

We cannot study the metals in a similar manner because they do not form stable hydrides. Let us instead compare the formulae of a series of salts derived from some acid, say

hydrochloric acid (HCl), by the replacement of the hydrogen by metals. We have—

(1) NaCl, KCl.
(2) $CuCl_2$, $MgCl_2$, $CaCl_2$, $ZnCl_2$, $BaCl_2$.
(3) $AlCl_3$, $FeCl_3$, $CrCl_3$.

The compounds in Group (1) are obviously derived from one molecule of hydrochloric acid, those in Group (2) from two molecules, and those in Group (3) from three molecules, because they contain respectively one, two, and three atoms of chlorine. It follows that—

(1) One atom of Na or K replaces *one atom* of H or combines with one atom of chlorine.

(2) One atom of Cu, Mg, Ca, etc., replaces *two atoms* of H or combines with two atoms of chlorine.

(3) One atom of Al, Fe, or Cr replaces *three atoms* of H or combines with three atoms of chlorine.

In other words, one atom of sodium or potassium possesses the same power of saturating the non-metal chlorine as one atom of hydrogen; one atom of Cu, Mg, etc., has the same saturating capacity as two atoms of hydrogen; and one atom of Al, Fe, or Cr as three atoms of hydrogen.

An examination of the compounds derived in a similar manner from other acids, *e.g.* sulphuric, nitric, and phosphoric acids, leads to like conclusions; we find, for instance, that one atom of sodium replaces one atom of hydrogen, and one atom of aluminium replaces three atoms of hydrogen, whichever acid is used.

Taking the atom of hydrogen as the standard, and calling its capacity to saturate other elements, or its *valency* unity, a number can be assigned to each element which expresses its saturation capacity or valency in terms of this unit. We may therefore define valency as follows:—**The valency of an element is represented by the number of atoms of hydrogen with which one atom of an element will combine, or which one atom of the element replaces.**

An element with a valency 1 is said to be *monovalent*, and the corresponding terms *divalent*, *trivalent*, etc., are applied

to elements whose valencies are respectively 2, 3, etc. Thus hydrogen, chlorine, and potassium are monovalent, oxygen and copper are divalent, nitrogen and aluminium are trivalent, and carbon is tetravalent. The valency is often represented by writing the necessary number in dashes or Roman numerals at the top right-hand corner of the symbol; thus H′, O″, N‴, C⁗, etc.

It must be added that certain metals, such as copper, iron, mercury, and tin, form two series of salts in which they show different valency. For instance, in $FeCl_2$ (ferrous chloride), iron is *divalent*, whilst in $FeCl_3$ (ferric chloride), iron is *trivalent*; in the same way we have *mercurous* chloride, HgCl, and *mercuric* chloride, $HgCl_2$, in which the valency of mercury is *one* and *two* respectively, and *stannous* and *stannic* chlorides ($SnCl_2$ and $SnCl_4$) in which the valency of tin is *two* and *four* respectively.

It may be noted in this connection that changes in the valency of a compound are brought about by oxidising and reducing agents (§ 98). Thus in the reactions—

$$2Fe''Cl_2 + HCl + HClO = 2Fe'''Cl_3 + H_2O$$
$$2Fe'''Cl_3 + SO_2 + 2H_2O = 2Fe''Cl_2 + 2HCl + H_2SO_4$$

it will be seen that oxidation usually involves an increase in the valency of an element, and reduction a decrease (§ 98).

The valencies of the majority of the elements, both metals and non-metals, can be found from a study of their *oxides* if we assume that oxygen is divalent. Let us examine the formulae of a number of oxides, *e.g.* :—

Na_2O, K_2O, Cl_2O, N_2O.
CuO, MgO, CaO, ZnO, BaO, PbO, FeO.
Al_2O_3, N_2O_3.
CO_2, SO_2, SiO_2.
N_2O_5, P_2O_5, I_2O_5.
SO_3.

We conclude that in these compounds, Na, K, Cl, and N (in N_2O) are monovalent; Cu, Mg, Ca, etc., are divalent; Al, N (in N_2O_3) are trivalent; C, S (in SO_2) and Si are tetra-

valent ; N (in N_2O_5), P (in P_2O_5), I (in I_2O_5) are pentavalent ; S (in SO_3) is hexavalent.

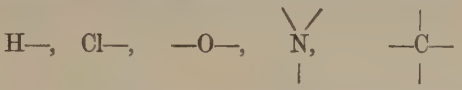
It will be observed that several of the non-metals, *e.g.* iodine, nitrogen, and sulphur, are capable of exerting a higher valency towards oxygen than towards hydrogen ; thus iodine is *monovalent* in HI and *pentavalent* in I_2O_5, nitrogen is *trivalent* in NH_3, and *pentavalent* in N_2O_5, sulphur is *divalent* in H_2S and *tetravalent* and *hexavalent* in SO_2 and SO_3 respectively. In general an element which is hexavalent may, in some of its compounds, be tetravalent or divalent, and one which is pentavalent may be trivalent or monovalent. It should be mentioned, however, that many elements exhibit both an odd and an even valency, contrary to the belief of the earlier chemists.

The valencies of a number of common elements are given in the following table :—

VALENCIES OF COMMON ELEMENTS.

Monovalent.	Divalent.	Trivalent.	Tetravalent.	Pentavalent.	Hexavalent.
H	Ba	Al	Sn (ic)	P (in PCl_5, etc.)	S (in SO_3, etc.)
Na	Sr	Cr	C	N (in N_2O_5, etc.)	
K	Ca	Fe (ic)	Si		
Ag	Mg	As (ous)	S (in SO_2, etc.)		
Hg (ous)	Zn	Sb (ous)			
Cu (ous)	Cd	Bi (ous)			
F	Co	B			
Cl	Ni	P (in PCl_3, etc.)			
Br	Pb	N (in NH_3, etc.)			
I	Hg (ic)				
	Cu (ic)				
	Fe (ous)				
	Mn (ous)				
	Sn (ous)				
	O				
	S (in H_2S, etc.)				

24. Structural Formulae.—In order to represent diagrammatically the way in which the valencies of the different elements in a compound mutually satisfy one another, lines or " bonds " are drawn from the symbol of the element. It must be clearly understood by the student that this is only a device ; no such lines actually exist. Thus, to show that the valencies of hydrogen, chlorine, oxygen, nitrogen, and carbon are respectively 1, 1, 2, 3, and 4, we may write them—



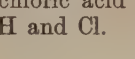
When an atom of chlorine unites with an atom of hydrogen their valencies mutually saturate one another, and the molecule of hydrochloric acid may be represented by drawing a line between H and Cl.

H—Cl.

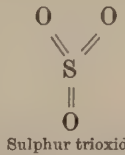
Again, when oxygen and hydrogen unite to form water, each of the two oxygen valencies saturates one hydrogen valency.

H—O—H.

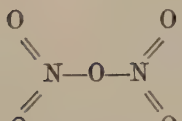
Similarly we may write :—



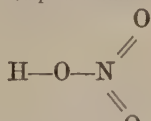
Sulphur dioxide.



Sulphur trioxide.



Nitrogen pentoxide.



Nitric acid

Formulae such as these, which show the way in which the atoms of a molecule are united together, *i.e.* show what other atom or atoms any given atom is combined with, are called *structural* or *graphic formulae.*

It must again be emphasised that the lines or bonds in such formulae have no real existence, they are merely graphical representations of chemical forces acting between the atoms.

25. Relation between Equivalent and Atomic Weight.— Suppose we wish to find the valencies of the three elements, Na, Mg, and Al, being given their atomic weights. The first thing to be done is to find their equivalents. Experiment shows that these are respectively 23, 12, and 9. The atomic weights are Na = 23, Mg = 24, and Al = 27. Also H = 1·008. We have then—

23 parts by weight of Na replace 1·008 parts by weight of H, *i.e.* 1 atom of Na replaces *one* atom of H.

12 parts by weight of Mg replace 1·008 parts by weight of H. $\therefore$ $2 \times 12 = 24$ parts by weight of Mg replace 2·016 parts by weight of H, *i.e.* 1 atom of Mg replaces *two* atoms of H.

9 parts by weight of Al replace 1·008 parts by weight of H. $\therefore$ $3 \times 9 = 27$ parts by weight of Al replace 3·024 parts by weight of H, *i.e.* 1 atom of Al replaces *three* atoms of H.

The valencies of Na, Mg, and Al are therefore 1, 2, and 3 respectively. It will be seen that in order to obtain the valency of an element, all we have to do is to divide the atomic weight of the element by its equivalent.

$$\text{Valency of Na} = \frac{23}{23} = 1,$$

$$\text{,, ,, Mg} = \frac{24}{12} = 2,$$

$$\text{,, ,, Al} = \frac{27}{9} = 3.$$

The following general relation between the atomic weight of an element and its equivalent may then be stated—

$$\text{Valency} = \frac{\text{Atomic Weight}}{\text{Equivalent}}.$$

Where an element has two equivalents and consequently two valencies, the equivalent and valency used in the above

formula must both apply to the same compound. Thus, considering the case of iron, its equivalent in ferrous chloride, $FeCl_2$, is 27·5 and its valency 2; in ferric chloride, $FeCl_3$, its equivalent is 18·5 and its valency 3. Both these sets of values should give the same atomic weight for iron on applying the formula—

(1) *Ferrous iron*—

$$2 = \frac{\text{Atomic Weight}}{28}.$$

$$\therefore \text{ Atomic Weight} = 2 \times 27{\cdot}5 = 55.$$

(2) *Ferric iron*—

$$3 = \frac{\text{Atomic Weight}}{18{\cdot}5}.$$

$$\therefore \text{ Atomic Weight} = 3 \times 18{\cdot}5 = 55.$$

26. Nomenclature of Compounds.—Compounds may be divided into two classes; those composed of *two elements* (called "binary" compounds), and those composed of *three or more elements*. The following points with regard to "names" should be particularly noted :—

(*a*) Binary compounds may be designated according to the number of atoms of the elements they contain, the number being usually stated only for the more non-metallic element, the termination of the name being -ide—

H_2O_2 hydrogen diox*ide*.
I_2O_5 iodine pentox*ide*.
PCl_3 phosphorus trichlor*ide*.
PCl_5 ,, pentachlor*ide*.

(*b*) Where only two compounds of the same elements exist, the termination **-ous** may be applied to the one with the smaller proportion of the more non-metallic element (the "lower" oxide, iodide, etc.), and the termination **-ic** to the other—

HgI mercur*ous* iodide; HgI_2 mercur*ic* iodide.
Cu_2O cupr*ous* oxide; CuO cupr*ic* oxide.

(*c*) Oxides, which when dissolved in water form acids, are termed "anhydrides," and these, together with the acids

they give rise to, receive the terminations **-ous** and **-ic** in the same sense as before—

N_2O_3, nitr*ous* anhydride or nitrogen trioxide ; HNO_2, nitr*ous* acid.
N_2O_5, nitr*ic* anhydride or nitrogen pentoxide ; HNO_3, nitr*ic* acid.
CO_2, carbon*ic* anhydride or carbon dioxide ; H_2CO_3, carbon*ic* acid.

(*d*) Salts take the termination **-ite** or **-ate** according as they are derived from *-ous* or *-ic* acids respectively—

H_2SO_3, sulphur*ous* acid ; Na_2SO_3, sodium sulph*ite*.
H_2SO_4, sulphur*ic* acid ; Na_2SO_4, ,, sulph*ate*.
$H_2S_2O_8$, *per*sulphuric acid ; $Na_2S_2O_8$, ,, persulph*ate*.

(*e*) Where more than two compounds of the same element exist further discrimination is necessary, and the prefix **hypo-** is applied to the lowest and **per-** to the highest—

HClO, *hypo*chlorous acid ; KClO, potassium hypochlor*ite*.
$HClO_2$, chlor*ous* acid ; $KClO_2$, ,, chlor*ite*.
$HClO_3$, chlor*ic* acid ; $KClO_3$, ,, chlor*ate*.
$HClO_4$, *per*chloric acid ; $KClO_4$, ,, perchlor*ate*.

QUESTIONS.—CHAPTER IV.

1. What do you understand by the *chemical equivalent* of an element ? Describe an experiment by which the equivalent of magnesium can be determined.

2. Describe in detail how you would proceed to find the chemical equivalent of copper by deposition of the metal, assuming the equivalent of zinc known.

3. How would you proceed to determine the equivalent of aluminium given a supply of the metal, some strong hydrochloric acid, and some water ?

4. Explain the term *valency*, illustrating your answer by examples.

5. Give examples of elements which exhibit more than one valency, and illustrate the way in which the composition of their compounds changes with the change in valency.

6. What is a *structural formula ?* Write down the structural formulae for ammonia, sulphur trioxide, and nitric acid.

7. What is the relation between the atomic weight, the equivalent and the valency of an element ? Give examples to illustrate your answer.

8. Explain the term *binary compound*, and give three examples of binary compounds.

CHAPTER V.

THE PHYSICAL PROPERTIES OF GASES.

27. Fundamental Properties of Gases (1) *Expansion and Compression.*—Unlike liquids and solids, gases have the property of expanding to an indefinite extent. Thus one litre of chlorine could be disseminated so that it was evenly spread all through the room, or it could be compressed to occupy a few cubic centimetres. Gases have a discontinuous structure, or in other words, are made up of gas particles and spaces. In expansion the size of the spaces increase, and in compression decrease. The particles of the gas are called **molecules,** and under the effect of pressure do not change their size. We may define the word "molecule" as the smallest particle in which the chemical properties of a substance are retained.

(2) *Elasticity.*—The Kinetic Theory states that gases consist of particles in motion in all directions (see *Inorganic Chemistry, Mainly Metals*). This motion causes the gas to exert a pressure in all directions due to the bombardment of the walls of the containing vessel. As this pressure does not alter with time, we assume that the molecules of the gas are perfectly elastic, for no energy is lost by the innumerable collisions.

28. Effect of Pressure : Boyle's Law.—Robert Boyle (1661) investigated the relation between the pressure and the volume of a gas, and found "the pressures and the expansions to be in reciprocal proportions." E. Mariotte, in 1675, repeated Boyle's work, and confirmed his results.

A simple experiment with a pop-gun will convince you that the volume of space taken up by a gas depends on its pressure. The effect can be investigated quantitatively by means of the following experiment :—

Exp. 13. The apparatus shown in Fig. 6 is used, and will be familiar to students. A contains air and B, together with the rubber tubing, contains mercury. By placing a scale behind A, and by lowering and raising B, the volume of air in A can be obtained under different pressures. To obtain the volume of air in A at atmospheric pressure, let the levels of mercury in A and B be equal. The pressure in A is equal to the atmospheric pressure plus or minus the length of the difference in the levels of A and B. Record the results in two columns; pressure and volume. It will be found that the product, pressure × volume, is constant, *i.e.* indicating pressure by P and volume by V, we have then PV is a constant.

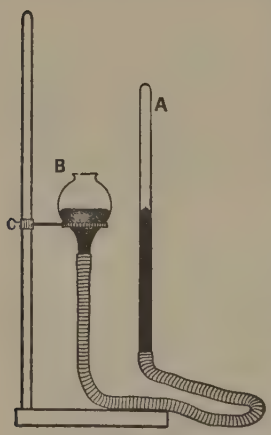


Fig. 6.

These results support the following statement, known as **Boyle's Law** : — *When the temperature remains constant the volume occupied by a gas varies inversely as the pressure, i.e.* :—

Pressure × Volume = a Constant,

$$PV = k.$$

29. Liquefaction of Gases.—Boyle's Law is only true for a perfect gas under moderate pressure and temperature. No perfect gas exists in reality, for though very many gases show a close agreement at such pressures and temperatures as occur in general practice, yet under extreme conditions even hydrogen, nitrogen, and those gases which behave most nearly like perfect gases, fail to show agreement, and at sufficiently low temperature and high pressure they change their condition and become liquid.

The following list gives the temperatures and pressures at which some of the commoner gases become liquids :—

Carbon dioxide at	− 80° C.	and	1 atmosphere pressure.
or at	− 20° C.	,,	23 atmospheres ,,
or at	+ 20° C.	,,	58 ,, ,,
Sulphur dioxide at	− 10° C.	,,	1 atmosphere ,,
or at	+ 10° C.	,,	2·3 atmospheres ,,
or at	+ 30° C.	,,	5·3 ,, ,,
Nitrogen at	− 195° C.	,,	1 atmosphere ,,
or at	− 160° C.	,,	14 atmospheres ,,
or at	− 146° C.	,,	35 ,, ,,
Air at	− 194·4° C.	,,	1 atmosphere ,,
or at	− 140° C.	,,	39 atmospheres ,,
Chlorine at	− 34° C.	,,	1 atmosphere ,,
or at	0° C.	,,	6 atmospheres ,,
Ethylene at	− 102·5° C.	,,	1 atmosphere ,,
Nitrous oxide at	0° C.	,,	30 atmospheres ,,

A gas cannot always be liquefied by pressure alone. There is, in fact, a temperature peculiar to each gas *above* which the gas cannot be liquefied by any pressure whatever. Thus Andrews has shown that at temperatures above 31° C. it is impossible to liquefy carbon dioxide by pressure.

This temperature is called the **critical temperature** of the gas, so that the critical temperature of carbon dioxide is 31° C. The pressure which a gas exerts at its critical temperature is called the **critical pressure**. The following table gives these two constants for a number of gases :—

CRITICAL TEMPERATURES AND PRESSURES.

Gas.	Critical Temperature.	Critical Pressure.
Nitrogen	− 146° C.	35 atmospheres.
Oxygen	− 118·8° C.	50·8 ,,
Nitric oxide ...	− 93·5° C.	71·2 ,,
Marsh gas	− 95·5° C.	50 ,,
Carbon monoxide ...	− 141° C.	36 ,,
Hydrogen	− 242° C.	15 ,,

It will be noticed that the six gases in the table have very low critical temperatures; these gases were, 50 years ago, called *permanent* gases, because until 1879 all attempts to liquefy them had failed owing to the temperatures employed being above the critical point.

Various methods have been employed in liquefying gases. Faraday was able to liquefy a large number of gases in glass tubes by means of their own pressure. To liquefy chlorine in this way a quantity of the yellow crystals of chlorine hydrate (a compound of chlorine and water) are brought into a glass tube of about 1 cm. in diameter, and closed at one end. The tube is then bent at right angles at about its middle point, and sealed. If now the sealed end be placed in a freezing mixture, whilst the other end containing the hydrate be gently warmed, a comparatively large volume of chlorine is liberated, and the pressure of the accumulated gas together with the low temperature employed is sufficient to bring about its liquefaction.

If silver chloride be saturated with ammonia gas, a compound of the two is formed, and this body treated in the same way evolves ammonia in such a quantity as to liquefy by its own pressure.

With many gases a much lower temperature is required than can be obtained by using an ordinary freezing mixture. Thus Pictet liquefied oxygen by submitting it to a very high pressure in a copper tube at — 140° C.

Other methods which are used will be referred to in the sequel.

30. Effect of Temperature. Charles's Law. The Law of Pressures.—Priestley, in 1790, found that carbon dioxide (fixed air) and air expand the same amount with the same degree of heat. His experiments were what he termed "coarse experiments." Gay-Lussac later, in 1802, after investigation, propounded the following statement: "The same rise of temperature produces in all gases the same increase in volume, provided the temperature be kept constant." This law is now known as Charles's Law, because J. A. C. Charles had made somewhat similar experiments on the subject fifteen years before Gay-Lussac.

The effect of temperature on the volume of air may be found by the following method :—

Exp. 14. Take a 250 c.cm. flask and tightly-fitting indiarubber cork, through which passes a piece of glass tubing of very narrow bore (capil-

ary tubing), bent twice at right angles as shown in Fig. 7. Immerse the flask up to the level of the cork in a beaker or tin vessel of hot water, clamping it in position so that there is, say, half-an-inch of water between the bottom of the flask and the beaker. Boil the water and keep it boiling for some five or ten minutes.

Now place a beaker with cold water so that the outlet of the capillary tube dips deeply into it. Raise the flask out of the hot water, keeping the outlet all the while dipping beneath the water in the beaker, and let it cool by standing in the air. Notice that water is driven from the beaker into the flask. Plunge the flask overhead into a mixture of water and ice, still keeping the outlet under water, and let it remain so long as water drips back into it through the capillary tube.

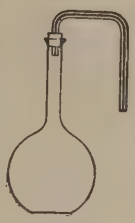


Fig. 7.

Take now a cylindrical measure graduated into cubic centimetres, and pour the water from the flask into it so as to ascertain how many cubic centimetres have flowed back into the flask. Call this v. Then measure how much water is needed to fill the flask up to the level of the lower surface of the cork. Call this V. Then V represents the volume of air which just fills the flask at 100° C. and $(V - v)$ the volume which this air occupies at 0° C., the temperature of ice-cold water. Therefore $(V - v)$ c.cm. of air at 0° C. expand v c.cm. on heating to 100° C.

The amount of expansion for 1° C. rise in temperature is $\frac{v}{100}$ c.cm.; therefore the expansion for 1° is $v \div (V - v)$ 100 of the whole. Calculate out from your results the value of this expression, and see how near it agrees with the number $\frac{1}{273}$.

This result can be incorporated in the generalisation known as **Charles's Law**, which is expressed thus :—*Equal volumes of all gases under the same pressure expand equally for equal increments of temperature.*

Experiments in which precautions were taken to secure great accuracy yielded the result that gases at 0° C. expand $\frac{1}{273}$ part of their volume for each increment of 1° C. Hence the mathematical statement of the law is :—

$$V_t = V_o + \tfrac{1}{273} V_o t \therefore V_t = V_o(1 + \tfrac{1}{273} t).$$

where V_o = volume at 0° C. and V_t = volume at t° C.

Thus for temperatures above zero we have—

273 volumes of gas at 0° C. become 274 vol. at 1° C.,
" " " 275 " " 2° C.,
" " " 276 " " 3° C.,

and so on.

For temperatures below zero, we should have—

273 volumes of gas at 0° C. become 272 vol. at − 1° C.,
" " " 271 " " − 2° C.,
" " " 270 " " − 3° C.,

and so on.

If the behaviour of gases remained the same at *very low* temperatures, we should find that 273 vol. at 0° C. would become *nil* at −273° C. But, long before such a low temperature is reached, most gases condense to liquids, and many even to solids.

In dealing with gases in practice, however, the chemist has usually only to concern himself with temperatures above zero and a few degrees below zero; and hence you will find it convenient to notice that *under the same pressure the volume of a gas is proportional to the temperature as reckoned, not from* 0° *C., as is generally done, but from* −273° C., termed *absolute zero.* We have thus :—

Temperature.	Absolute Temperature.	Volume.
0° C.	273	273
10° C.	283	283
− 10° C.	263	263

and so on. Or calling T_1 and T_2 the absolute temperatures corresponding to t_1° C. and t_2° C. (*i.e.* $T_1 = 273 + t_1$ and $T_2 = 273 + t_2$), and V_1 and V_2 the volumes of a given mass of gas at these temperatures, the pressure being the same in both cases, then—

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}.$$

The **Law of Pressures** may be briefly referred to in passing. If the volume of a given mass of gas be kept constant while the temperature is raised, the pressure will evidently increase. Experiment shows that *the pressure increases by* $\frac{1}{273}$ *of the pressure at* 0° *C. for each increment of* 1° *C. in temperature.* Hence, as in the case of Charles's Law, we have—

$$P_t = P_o\left(1 + \frac{1}{273}t\right) \text{ and } \frac{P_1}{P_2} = \frac{T_1}{T_2}$$

where P_t = pressure at t° C. P_o = pressure at 0° C., P_1 =

pressure at absolute temperature T_1 and P_2 = pressure at absolute temperature T_2. This is the Law of Pressures. Note that the volume is kept constant while the temperature (and therefore the pressure) is changed.

31. Correction for Temperature and Pressure.—By combining the gas laws previously considered we may obtain the following general **gas equation** (see *Inorganic Chemistry, Mainly Metals*) :—

$$PV = RT.$$

Where P = pressure, V = volume, T = absolute temperature, and R is a constant.

It should be again noted that in Boyle's Law ($PV = k$) the temperature is kept constant while P and V are changing; in Charles's Law ($V_1/V_2 = T_1/T_2$) the pressure is kept constant while V and T are changing; and in the Law of Pressures ($P_1/P_2 = T_1/T_2$) the volume is kept constant while P and T are changing. When temperature, pressure, and volume are all changing we have the gas equation PV/T = a constant = R.

As the volume of a given quantity of gas varies with both the pressure and the temperature, in order that results of chemical experiments involving gases may be compared together, we must all agree to state our results as they would be if they were all performed under the same conditions as to temperature and pressure. It has been agreed, therefore, that the temperature for such reference shall be the freezing-point of water (0° C.), and the normal or average pressure of the atmosphere, equal to that of a column of mercury 760 mm. in height. These standard conditions are referred to as "Normal temperature and pressure," and the expression is often abbreviated to the letters "N.T.P."

Suppose that in an experiment you prepare 233 c.cm. of a gas, the temperature of the atmosphere being 15° C. and the pressure 775 mm. of mercury. Let us reduce the volume of gas evolved to standard conditions. We have—

$$0° \text{ C.} = 273° \text{ absolute.}$$
$$15° \text{ C.} = 273 + 15 \text{ or } 288° \text{ absolute.}$$

Therefore by Charles's Law the volume will be decreased in the ratio $\frac{273}{288}$ when reduced to 0°.

Again, by Boyle's Law the volume will be increased in the ratio $\frac{775}{760}$ when reduced to 760 mm.

Applying both corrections we have for the volume at 0° C. and 760 mm.—

$$233 \times \frac{273}{288} \times \frac{775}{760} \text{ or } 225 \text{ c.cm.}$$

The formula which can be used in calculations which involve variations in the volumes of gases owing to changes in temperature and pressure is—

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2},$$

in which P, V, and T have the usual meaning. This, of course, is merely another way of writing the gas equation.

Thus in the example above $P_1 = 775$, $T_1 = 288$, $T_2 = 273$, $P_2 = 760$, $V_1 = 233$, it is required to find V_2—

$$\frac{775 \times 233}{288} = \frac{760 \times V_2}{273}.$$

32. Density and Relative Density (or Specific Gravity) of Gases.—By the *density* of a gas we mean the *mass of it which occupies unit volume*. The most convenient volume to take as the unit is 1 *litre*. A very simple experiment will convince you that the densities of different gases vary very much.

Exp. 15. Take a large beaker and suspend it from one arm of a rough balance. Add weights to the other scale-pan till the balance is in equilibrium. Now prepare some carbon dioxide and pour it into the beaker; the arm to which the beaker is attached at once *sinks*, showing that carbon dioxide has a greater density than air.

Now repeat the experiment, but hang the beaker in an inverted position and pour hydrogen *up* into it; the arm to which the beaker is attached *rises*, showing that the density of hydrogen is less than that of air.

Since hydrogen is the least dense of all gases it is very common to state the *relative density* (or specific gravity) of a gas in terms of hydrogen as unity, instead of stating the density as defined above. The *relative density* of a gas (in terms of hydrogen as unity) may be defined as the *weight of a given volume of the gas divided by the weight of an equal volume of hydrogen under the same conditions of temperature and pressure.* Sometimes relative densities are given in terms of *air* as unity.

Density of Air.—The density of air may be determined approximately in the following manner :—

Exp. 16. Fit a strong flask, holding about 300 c.cm., with a cork through which passes a short length of glass tubing. Attach to it a piece of rubber tubing carrying a clip. Place about 30 c.cm. of water in the flask, open the clip, and boil the water for ten minutes. The steam drives out all the air. Close the clip, remove the flame at once, allow to cool, and weigh the flask and its contents (w_1).

Now open the clip carefully so as to allow air to enter gradually. When no more air enters weigh again (w_2), and measure the volume of water that remains (v_1). Finally, fill the flask with water to the level of the cork, and measure the volume of this water (v_2).

Let $t°$ be the temperature of the air.

Let H be the barometric height in millimetres of mercury.

$(v_2 - v_1)$ c.cm. is the volume of air at $t°$ and H mm. that (together with the v_1 c.cm. of water) filled the flask.

$(w_2 - w_1)$ grm. is the weight of this air.

The volume at N.T.P. is $(v_2 - v_1) \times \frac{H}{760} \times \frac{273}{273 + t} = v$ say.

Therefore the mass of 1 litre at N.T.P. is $\left(\frac{w_2 - w_1}{v} \times 1000\right)$ grm.

Calculate out your result and see how near it agrees with the value 1·293 grm., which accurate measurements have shown to be the correct density of dry air. Your result cannot be quite correct because the air filling the flask is *moist*, not *dry*. Note that the above gives the *density* in *grammes per litre* at N.T.P.

Density and Relative Density of Carbon Dioxide.—The density of carbon dioxide can be calculated from the following results :—

In an Experiment 1 grm. of chalk gave 225 c.cm. of carbon dioxide measured at N.T.P.

In another Experiment 1 grm. of chalk gave 0·445 grm. of carbon dioxide.

∴ 225 c.cm. of carbon dioxide measured at N.T.P. weigh 0·445 grm.

∴ 1000 c.cm. or 1 litre of carbon dioxide measured at N.T.P. weigh $1000 \times \frac{0{\cdot}445}{225}$ or 2 grm. Thus the *density* of carbon dioxide at N.T.P. = 2 grm. per litre.

Again, 1 litre of hydrogen at N.T.P. has been found to weigh 0·09 grm.

∴ the density of carbon dioxide relative to hydrogen, *i.e.* its *relative density*, using hydrogen as the standard, is about $\frac{2}{0{\cdot}09}$ or 22.

Note particularly that the first result above is worded "density of carbon dioxide at N.T.P. = 2 *grm. per litre*": the second result is worded "relative density or specific gravity of carbon dioxide (hydrogen as standard) = 22."

33. Diffusion of Gases. Graham's Law.—The phenomenon of the mixing of gases is called **gaseous diffusion.**

Although Graham in 1851 was the first to measure the rates of diffusion of gases, Parrot had noticed the phenomenon of diffusion in 1815. Graham later extended his work to deal with the diffusion of dissolved bodies through animal membranes. The method by which the Law of Gaseous Diffusion was established consisted in accurate experiments on the rate of escape of gases through a porous plug made of plaster of Paris ($CaSO_4$), into a partial vacuum.

The difference in the rates of diffusion can be used to separate one gas from another. Thus if a mixture of hydrogen and oxygen be passed through the stem of a "church-warden" pipe, the end of which leads under a beehive shelf in a pneumatic trough, and the issuing gas collected, it will be found to be mainly oxygen. The hydrogen has diffused through the porous stem whilst the oxygen has passed on to be collected. Graham called this phenomenon *Atmolysis*.

We may define **Graham's Law of Gaseous Diffusion** as

follows :—**the relative rates of diffusion of gases are inversely proportional to the square root of their densities.** The same law applies also to the *Effusion* of gases, or the rate of flow through a tiny hole in a metal plate. Thus in relation to air—

		$\frac{1}{\sqrt{\text{density}}}$.	Velocity of diffusion observed.
Density of hydrogen	= 0·0695	= 3·792	3·830
,, carbon dioxide	= 1·5180	= 0·812	0·812

The phenomenon of gaseous diffusion can be investigated by the student in the following experiments :—

Exp. 17. A porous cell, such as is used in voltaic batteries, is fitted with an indiarubber stopper, and a glass tube about half-a-metre long, furnished with a bulb, is passed through the stopper ; this is bent and

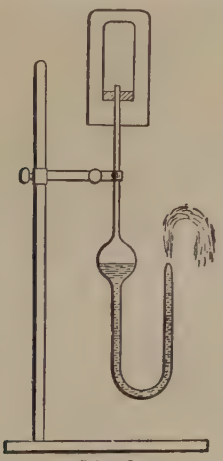


Fig. 8.

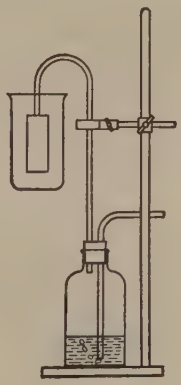


Fig. 9.

drawn out into a jet, as shown in Fig. 8. Before inserting the cork fill the bulb and lower part of the tube with water. Now place a beaker filled with hydrogen over the porous cell, and the water will be immediately depressed and driven out of the jet in a fine stream.

This is evidence that the light gas hydrogen passes through the walls into the porous cell quicker than the air is able to pass out of it. A

greater volume of gas collects within the space of the cell and tube and forces the water out before it.

Now perform a similar experiment, using in place of hydrogen a gas heavier than air—say carbon dioxide.

Exp. 18. Fit up the apparatus shown in Fig. 9. In this case the glass tube carrying the porous cell is bent round so that a beaker containing the carbon dioxide may be in an upright position when placed over the cell. The bottle contains a little water. When the beaker is placed in position bubbles of air pass up through the liquid in the bottle.

The explanation is that air diffuses out of the cell quicker than the heavier gas, carbon dioxide, passes into it. This tends to produce a partial vacuum, and air enters through the delivery tube dipping into the liquid to take its place. The relative densities of the gases employed in the above experiments are—

Hydrogen, 1. Air, 14·4. Carbon dioxide, 22.

We see then that the smaller the density of a gas the more rapidly it diffuses.

34. Combination of Gases by Volume. Gay-Lussac's Law.—Cavendish showed that hydrogen and oxygen united by volume in the ratio of 2 : 1 *approximately*. Gay-Lussac, in 1808, showed that 100 parts by volume of oxygen united with 199·89 parts by volume of hydrogen, a result which very closely agrees with the correct ratio 1 : 2. The same investigator studied the combining volumes of many other gases. Thus he found that—

(*a*) 2 vol. of carbon monoxide combine with 1 vol. of oxygen to form 2 vol. of carbon dioxide.

(*b*) 1 vol. of nitrogen combines with 3 vol. of hydrogen to form 2 vol. of ammonia.

(*c*) 1 vol. of hydrogen combines with 1 vol. of chlorine to form 2 vol. of hydrochloric acid gas.

Gay-Lussac's actual experimental analysis did not give these exact ratios, but he rightly concluded that the small deviations from the exact ratios were due to experimental errors. He then stated the **Law of Combining Volumes,**

which bears his name : **When gases combine together they do so in volumes which bear a simple ratio to one another and to that of the product if gaseous.**

35. Dalton's Law of Partial Pressures.—We have seen that when gases are brought together, they mix intimately by diffusion, that is, provided they do not react together chemically. Dalton, in 1802, found that in a mixture of gases each gas asserted the same pressure as if it occupied the whole space alone, and that the total pressure of the mixture was the sum of the individual pressures of the components of the gaseous mixture.

Thus if a gas is collected over water, the space occupied by the gas is also saturated with water vapour. The total pressure of the gas is therefore made up of two pressures—

(1) The pressure of the gas itself.

(2) The pressure of the water vapour.

In order to get the true volume of the gas we must therefore correct for the " pressure of aqueous vapour," *i.e.* for (2). It is known that the pressure of water vapour in contact with liquid water is constant for a constant temperature, and tables have been made which give the vapour pressure of water at different temperatures, and from them we can read off the partial pressure due to the water vapour. The true pressure of the gas is therefore the atmospheric pressure minus the vapour pressure of water at the temperature concerned. The student will find examples of this in Chapter X.

We may define **Dalton's Law of Partial Pressures** as follows :—**In a mixture of gases the total pressure of the mixture is equal to the sum of the partial pressures of the gases present.**

36. Solubility of Gases.—There is no general connection between the solubility of gases and their chemical composition. The very soluble gases are all, however, acid or alkaline in presence of water. Some gases, such as nitrogen, hydrogen, and carbon monoxide, are very slightly soluble, whilst others, such as ammonia, sulphur dioxide, and hydrogen chloride, are very freely soluble in water. The solubility, instead of

increasing with the temperature, as in the case of solids, *decreases*, though in no simple relation. One volume of water at the temperatures stated, and under 760 mm. pressure, dissolves the volumes of the respective gases given in the following table :—

Gases.	0° C.	10° C.	20° C.
Nitrogen	0·023	0·019	0·015
Oxygen	0·049	0·038	0·031
Hydrogen	0·021	0·019	0·018
Carbon dioxide	1·713	1·194	0·878
Sulphuretted hydrogen ...	4·621	3·362	2·554

As instances of much more soluble gases we may take—

Gases.	0° C.	10° C.	20° C.
Sulphur dioxide	79·8	56·6	39·4
Hydrochloric acid	525·2	473·9	442·0
Ammonia	1305·0	916·0	715·0

Methods of Measuring the Solubility of Gases.—The solubility of a moderately soluble gas such as carbon dioxide can be determined as follows. The apparatus, which is a modified form of that used by Heidenhain and Meyer is shown in Fig. 10. F is a Hempel's burette to which is connected a pipette A, by means of metal tubing E. A measured volume of water is placed in the pipette A. The gas, whose solubility is to be determined, is introduced into F by means of the three-way cocks B and G, and by raising and lowering the levelling tube D.

The next step consists in introducing a certain volume of the gas into the pipette A. This is performed by opening the cock H and at the same time opening G so that the measuring burette F and A communicate. The pipette is now well shaken until the water is saturated and a state of equilibrium is reached, and the mercury in the burette and the levelling

tube is at a constant level. The level of the water in the pipette is then brought to its former level by opening the lower tap under mercury, and lowering D.

The volume of gas remaining can now be determined, and hence the volume of gas absorbed by the amount of water in the pipette at a known temperature and barometric pressure is thus found. By keeping F and A at a fixed temperature the solubility may be determined for that temperature. Also the solubility of a gas in any liquid such as alcohol, can be found by placing alcohol instead of water in A.

For a gas which is very soluble in water a chemical method is usually applied. The gas is passed for a long time through a known volume of water kept at a constant temperature. When the water is saturated, the barometric pressure is taken, and the amount of gas absorbed by the water is determined by means of volumetric analysis.

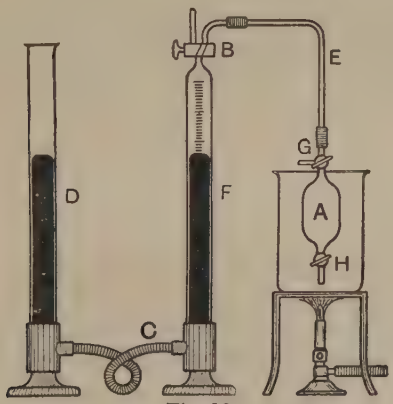


Fig. 10.

37. The Influence of Pressure on the Solubility of Gases. Henry's Law.—The relation between the pressure and the solubility was discovered by Henry in 1803. **Henry's Law**

may be defined as follows :—**The weight of a given gas which dissolves in unit volume of a given liquid is directly proportional to the pressure of the gas.** Thus 1 c.cm. of water at 0° C. dissolves the following weights of carbon dioxide :—

At 1 atmosphere	pressure	0·0356	grm.
„ 2 atmospheres	„	0·0713	„
„ 4 „	„	0·1426	„
„ ½ atmosphere	„	0·0178	„
„ ¼ „	„	0·0119	„

Soda-water is water charged with carbon dioxide under a pressure of about 4 atmospheres, and so long as this pressure on the surface of the water is maintained this volume of gas will be retained, but directly the pressure is released an effervescence is observed, and gas escapes from the liquid in proportion to the diminution of pressure.

38. Coefficient of Absorption.—The **coefficient of absorption** of a gas is defined as follows :—*The volume of a gas reduced to* 0° *C. absorbed by* 1 *c.cm. of a liquid at* $t°$ *C.* is called the *coefficient of absorption* of the gas in the liquid at $t°$ *C.*

Let v = Vol. of gas absorbed at $t°$ C

V = Vol. of liquid.

Then $v \times \frac{273}{273 + t}$ = Vol. of gas at 0° C.

$\therefore\ v \times \frac{273}{273 + t} \div V$ = Coeff. of absorption of the gas at $t°$ C.

The coefficients of absorption of carbon dioxide in water at 0° C. and 10° C. respectively are 1·799 and 1·185.

39. Solution of Mixed Gases.—At 0° C. and standard pressure a litre of water will dissolve 41 c.cm. of oxygen. If, however, we mix another gas, say nitrogen, with the oxygen, a smaller volume of oxygen (reduced to standard pressure) will be found to dissolve, a volume, indeed, proportional to the pressure of the oxygen alone (Dalton's Law of

Partial Pressures). In the same way the nitrogen will no longer dissolve to the extent of 20 c.cm. (see table), but to a smaller extent, in proportion to the pressure due to the nitrogen alone. For mixed gases, therefore, solution takes place in accordance with (*a*) the solubility of the gas in question, (*b*) the pressure exerted by it independently of any other gas or gases that may be present in the mixture.

Let us consider the important case of the solution of air (taken as 79 vol. of nitrogen* and 21 of oxygen) in water—

The oxygen dissolved by a litre of water from air will, according to this law, be, not 41 c.cm., but

$$\frac{41 \times 21}{100}, \text{ or } 8{\cdot}6 \text{ c.cm. per litre.}$$

The nitrogen dissolved will be, not 20 c.cm., but

$$\frac{20 \times 79}{100}, \text{ or } 15{\cdot}8 \text{ c.cm. per litre.}$$

So that in consequence of its greater solubility the proportion of oxygen to nitrogen dissolved in water is 8·6 : 15·8, and is therefore 35 per cent. of the whole. Air expelled from solution in water by boiling or by exposure to a vacuum is, then, much richer in oxygen than ordinary air.

So taking 0·04 as the normal percentage of carbon dioxide in air, this gas will be dissolved, not to the extent of 1,799 c.cm. to the litre, but to—

$$\frac{1799 \times 0{\cdot}04}{100}, \text{ or } 0{\cdot}72 \text{ c.cm. per litre.}$$

Now 1 litre of water dissolves $8{\cdot}6 + 15{\cdot}8 + 0{\cdot}72 = 25{\cdot}12$ c.cm. of oxygen + nitrogen + carbon dioxide from the air. Of this, carbon dioxide constitutes $\frac{0{\cdot}72}{25{\cdot}12} \times 100 = 2{\cdot}87$ per cent. Air dissolved in water is therefore, $\frac{2{\cdot}87}{0{\cdot}04} = 71\frac{3}{4}$ times as rich in carbon dioxide as the original air taken.

* Argon is here reckoned as nitrogen.

QUESTIONS.—CHAPTER V.

1. Enunciate Boyle's Law. Describe an experiment which illustrates it.

2. What do you understand by *absolute zero* and *absolute temperature ?*

3. State Charles's Law, and describe how you would prove it experimentally.

4. How would you proceed to find the density of carbon dioxide ?

5. Describe how you would proceed to measure the volume of hydrogen evolved from 0·1 gramme of magnesium by the action of sulphuric acid.

6. How would you proceed to estimate (1) the mass, (2) the volume of oxygen evolved on heating .1 grm. of red lead till decomposition was complete ?

7. Describe experiments to illustrate the phenomenon of *diffusion of gases* and state Graham's Law concerning the rate of diffusion.

8. State *Gay-Lussac's Law of Combination of Gases by Volume*, and illustrate it by examples.

9. State Henry's Law. What do you understand by the term *absorption coefficient* of a gas ?

10. Enunciate Dalton's Law of Partial Pressures.

11. How would you find the solubility of carbon dioxide in water at 20° C. ?

CHAPTER VI.

AVOGADRO'S HYPOTHESIS. ATOMIC AND MOLECULAR WEIGHTS.

40. Avogadro's Hypothesis.—After Dalton had propounded his Atomic Theory he was led to investigate the weights of atoms and "compound atoms." He also thought about the arrangement of the atoms in a definite volume of a gas. Dalton soon found that it was impossible to determine the weights of atoms, and then decided to find the relative weights of atoms, choosing as his unit the lightest atom, hydrogen. In 1802 Dalton put forward the idea that the spaces occupied by atoms were all equal, and hence that a given volume of all gases under the same conditions of temperature and pressure contained the same number of atoms. This theory had to be abandoned because, he said, on the combination of gases a decrease in volume should occur since the number of particles is reduced; and also that the density of the gas should therefore be increased. Dalton showed experimentally that neither of these results was obtained.

Berzelius also held the same view, but Gay-Lussac's Law of Volumes showed that the theory was inconsistent for the following reason:—Consider the combination of hydrogen and chlorine to form hydrochloric acid gas. *One* volume of hydrogen combines with one volume of chlorine to form *two* volumes of hydrochloric acid gas. Let x = number of particles of hydrochloric acid gas in *two* volumes; then by the hypothesis *one* volume of hydrogen will contain $\frac{x}{2}$ atoms of hydrogen and *one* volume of chlorine $\frac{x}{2}$ atoms of chlorine. Now let us take as two volumes such a volume that $x = 1$ (since we can, of course, take any volume we choose). Then $\frac{x}{2} = \frac{1}{2}$.

In other words, one particle of hydrochloric acid gas (contained in two volumes) is produced by the union of half an atom of hydrogen (contained in one volume) and half an atom of chlorine (contained in one volume). But, according to Dalton's theory, an atom cannot be divided; hence the hypothesis is incorrect.

The problem was solved by the Italian physicist Avogadro, who recognised two kinds of ultimate particles—

(*a*) The ultimate particle which can exist in the free state, as, for instance, the smallest particle of gaseous hydrochloric acid or of hydrogen. This he termed the *molecule*.

(*b*) The ultimate particle which is capable of taking part in a chemical change or capable of being transferred from one chemical compound to another, as, for instance, the hydrogen or the chlorine contained in the molecule of hydrochloric acid gas. This is termed the *atom*.

A molecule of a compound must necessarily contain at least two atoms. A molecule of an element may contain one or more atoms.

Avogadro then restated the hypothesis which had been shown to be untenable as follows :—**Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.** This is referred to as **Avogadro's Hypothesis.**

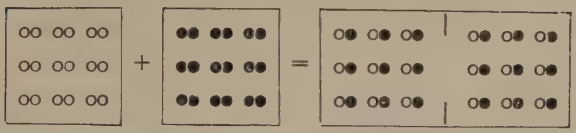
Thus Avogadro removed the difficulty Dalton had found in applying this theory, by suggesting that the molecules of an elementary gas might be built up of groups of similar atoms.

Let us return to the above example, namely, the combination of hydrogen and chlorine to form hydrochloric acid gas, and reconsider it in the light of Avogadro's hypothesis. We will make the assumption that the molecules of hydrogen and chlorine are each composed of two atoms,* and that a molecule of hydrochloric acid gas is composed of one atom of hydrogen and one atom of chlorine. Further, we will consider the combination of *nine* molecules of each gas (any other number

* There are very good grounds for this assumption, but we cannot stop to consider them here.

would do equally well). Then, assuming Avogadro's hypothesis, the combination may be represented as below, where

○ represents an atom of hydrogen.
○○ „ a molecule of „
● „ an atom of chlorine.
●● „ a molecule of „



Nine molecules or 1 volume. Nine molecules or 1 volume. Eighteen molecules or 2 volumes.

But this agrees with the results of experiment : *i.e.* Avogadro's hypothesis harmonises Gay-Lussac's Law and Dalton's Atomic Theory as far as the combination of hydrogen and chlorine is concerned. Similarly the hypothesis affords a satisfactory explanation of the volumetric relations of the other gases.

41. Molecular and Atomic Weights.—We have defined an atom to be the smallest particle of an element that can take part in a chemical change. Similarly the molecule is the smallest particle of an element or compound which can normally lead a separate existence. In some cases the gaseous molecule is found to consist of one atom and is termed *monatomic*. Molecules containing two atoms are called *diatomic*; similarly the terms *triatomic*, *tetratomic*, *polyatomic* are used. The table below indicates the number of atoms in the molecules of some elements.

Monatomic	Na, K, Zn, Cd, Hg, Argon Group, S, Sb.
Diatomic.	H_2, N_2, O_2, Halogens, S_2, As_2, Sb_2.
Triatomic.	O_3.
Tetratomic.	P_4, As_4. Sulphur is octatomic, S_8.

The standard by which the weights of atoms and molecules are expressed is the weight of the oxygen atom, which is taken

as 16, when hydrogen equals 1·008. *The atomic weight of an element is thus the number of times its atom is heavier than $\frac{1}{16}$ of the atom of oxygen. The molecular weight of an element or compound is the number of times its molecule is heavier than $\frac{1}{16}$ of the atom of oxygen.* As the atomic weight of oxygen is fixed at 16, it is clear that atomic and molecular weights are merely *ratios* and not the actual weight in grammes of these. The methods of determining atomic and molecular weights are described in *Inorganic Chemistry, Mainly Metals.*

42. Relation of Molecular Weight of Gases to Density.—The weight of the molecule of a substance, *i.e.* its *molecular weight*, is of course equal to the sum of the weights of the individual atoms contained in the molecule, and like them is expressed in terms of the weight of an atom of hydrogen as unity. As a molecule of hydrogen is represented by the formula H_2, the molecular weight of hydrogen is $2 \times 1{\cdot}008$ or $2{\cdot}016$.

Now since from Avogadro's hypothesis (§ 40) equal volumes of gases contain an equal number of molecules, it follows that the weights of the molecules of different gases are in the same ratio as the weights of equal volumes of the gases, i.e. *their molecular weights are proportional to their densities.*

Now the density of hydrogen is usually taken as unity, and we saw above that its molecular weight is 2; hence its molecular weight is numerically twice its density. Further, since, as we have just seen, the molecular weights of gases are proportional to their densities, it follows that the *molecular weight of any gas is numerically twice its density referred to hydrogen as unity.*

43. Symbols, Formulae, and Equations. Historical.—The alchemists had symbols to represent different substances. Thus the sun, ☉ or ☼, represented gold, and the moon ☾, represented silver. Lavoisier adopted a triangle ▽ for water and ⊕ for oxygen. Dalton, however, used a symbolic notation of circles: thus ○ represented oxygen, ⊙ hydrogen, ⓝ nitrogen, ● carbon. Compounds were represented by a combination of these; water was ⊙○ (he believed water to be HO), carbon dioxide was ○●○. Berzelius, who said this

system was unwieldy and cumbersome, changed it to the one we now use.

It was not for many years after this, however, that chemists were agreed on the formulae of *compounds*. Thus Berzelius used $\dot{H}O$ for water, whilst Gmelin used HO. Hence in 1860 different textbooks of chemistry wrote the formula for water in the following ways :—H_2O, $\dot{H}O$, HO, and H_2O_2 ; similarly marsh gas was written CH_4, $C_2\dot{H}_4$ or C_2H_4. In the same year a meeting of about one hundred of the most famous chemists in the world took place at Karlsruhe, to discuss these anomalies. The solution was due mainly to Cannizzaro, who insisted that the basis for the determination of formulae and the atoms in the molecule should be Avogadro's Hypothesis.

Symbols.—In many cases the initial letter of the name of an element is the *symbol* used to represent it : *e.g.* hydrogen is represented by H and oxygen by O. When the names of two or more elements commence with the same letter, two significant letters are used—the first and one other ; one of the elements may, however, be represented by the initial letter only. For example, the names of four elements commence with B—barium, bismuth, boron, and bromine ; the symbols for these elements are Ba, Bi, B, and Br respectively. Some chemical symbols are derived from the Latin names of the elements they represent : thus copper is represented by Cu (Lat. *cuprum*), iron by Fe (Lat. *ferrum*), potassium by K (Lat. *kalium*), mercury by Hg (Lat. *hydrargyrum*), and sodium by Na (Lat. *natrium*).

The symbol for an element is taken to mean not *any* quantity of that element, but a quantity proportional to the atomic weight of the element. Thus C stands for 12 parts by weight of carbon and O for 16 parts by weight of oxygen. When the number of atoms in a molecule of an element is known, the molecule is represented by placing a small number below and to the right of the symbol for the element : *e.g.* a molecule of oxygen is represented by O_2, since we know that the molecule contains two atoms.

Formulae.—Similarly, instead of the names of compounds, we often use *formulae* which indicate the composition of the

bodies. The formula of a compound is built up by placing the symbols for the elements of which it is composed in juxtaposition, and adding suffixes to indicate the relative number of atoms of each element present. Thus carbon dioxide is represented by the formula CO_2, which means that one atom, *i.e.* 12 parts by weight, of carbon is united with two atoms, *i.e.* 32 parts by weight, of oxygen. Again, the formula for water is H_2O, and implies that two atoms, *i.e.* 2 parts by weight, of hydrogen are united with one atom, *i.e.* 16 parts by weight, of oxygen.

Equations.—A *chemical equation* is an equation which represents by means of symbols the nature and relative amounts of the bodies concerned in a chemical change.

Certain chemical substances being brought together under suitable conditions, a chemical change takes place by which one or more of the constituents is set free or transferred, the state before and after the change being separated by =.

As instances of such equations we may give the action of hydrogen at red heat on oxide of copper—

$$\underset{\text{Hydrogen.}}{H_2} + \underset{\text{Copper oxide.}}{CuO} = \underset{\text{Water.}}{H_2O} + \underset{\text{Copper.}}{Cu}$$

and the action of zinc on dilute sulphuric acid—

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2}.$$

Such equations may be interpreted quantitatively according to the atomic weights given in the Appendix. Thus in the first case $2 \times 1{\cdot}008$ or $2{\cdot}016$ parts by weight of hydrogen will effect the reduction of $63{\cdot}1 + 15{\cdot}88$ or $78{\cdot}98$ parts by weight of oxide of copper yielding $2 \times 1{\cdot}008 + 16 = 18{\cdot}016$ parts by weight of water and $63{\cdot}1$ parts by weight of copper. In the second case $64{\cdot}9$ parts by weight of zinc acting upon $2 \times 1{\cdot}008 + 31{\cdot}8 + 4 \times 16$ or $97{\cdot}81$ parts by weight of sulphuric acid yield $64{\cdot}9 + 31{\cdot}8 + 4 \times 16$ or $160{\cdot}7$ parts by weight of zinc sulphate and $2{\cdot}016$ parts by weight of hydrogen.

In writing equations to express chemical reactions, regard must be paid to the state in which the bodies concerned

exist. The molecular composition of a substance in the *solid* condition is usually unknown, and a mere empirical statement of the quantity of the substance taking part in the reaction must be made. This is also frequently the case when a substance is in the *liquid* state, but when it is in the *gaseous* state the molecular composition is known and must be indicated.

2 S and S_2 both represent 64 parts by weight of sulphur. The first is the form used for expressing a certain weight of solid sulphur ; the second expresses the same weight of sulphur in the form of vapour at a high temperature, it being known that the molecule of sulphur at high temperature is composed of two atoms. Again—

$$H_2 + O = H_2O$$
$$KClO_3 = KCl + O_3$$

would both be incorrect, since in the first equation free oxygen is employed, and we have learnt that in this state there are two atoms in the molecule, and in the second equation O_3 would indicate that ozone was the gas resulting from the decomposition of $KClO_3$ (since the molecule of ozone is composed of three atoms of oxygen) : this is not the case. The correct form of both expressions would be obtained by doubling the equations thus—

$$2\,H_2 + O_2 = 2\,H_2O$$
$$2\,KClO_3 = 2\,KCl + 3\,O_2.$$

44. How to Work Out an Equation.—It will be useful to discuss the mode of arriving at the equations which express the reactions taking place. Let us take the case of the reduction of potassium permanganate by sulphur dioxide. We know that the substances we start with are $KMnO_4$, SO_2, and water, and the products are acid potassium sulphate, $KHSO_4$ (not the normal sulphate, because free sulphuric acid is produced), manganese sulphate, $MnSO_4$, and free sulphuric acid.

Now potassium permanganate may be considered as made up of the two oxides, K_2O and Mn_2O_7 ($K_2O + Mn_2O_7 =$

$K_2Mn_2O_8 = 2\ KMnO_4$), and manganese sulphate of MnO and SO_3.

We may therefore represent the reduction of potassium permanganate to manganese sulphate by reference to the corresponding oxides of manganese, thus—

$$Mn_2O_7 \rightarrow 2\ MnO + 5\ O.$$

But Mn_2O_7 corresponds to two molecules of potassium permanganate, and therefore *two molecules of* $KMnO_4$ *yield five atoms of oxygen available for oxidising purposes, i.e.* of so-called "available oxygen." Further, one molecule of sulphur dioxide requires one atom of oxygen to convert it into sulphur trioxide, the oxide corresponding to sulphuric acid; consequently 5 atoms of oxygen will oxidise 5 molecules of sulphur dioxide.

We can now write down the left-hand side of the equation with the exception of an unknown quantity of water, say x molecules—

$$2\ KMnO_4 + 5\ SO_2 + xH_2O = \quad .$$

Now since the potassium goes to $KHSO_4$ and the manganese to manganese sulphate, the right-hand side of the equation may be written—

$$= 2\ KHSO_4 + 2\ MnSO_4 + yH_2SO_4,$$

where y has to be determined.

It is easy to see that $y = 1$, for only one atom of sulphur of the $5\ SO_2$ remains to be accounted for. So far then we may write the equation—

$$2\ KMnO_4 + 5\ SO_2 + xH_2O = 2\ KHSO_4 + 2\ MnSO_4 + H_2SO_4.$$

But on the right side of the equation we have four atoms of hydrogen, and in order that the left-hand side may have the same number we must make $x = 2$. The correct equation is, therefore—

$$2\ KMnO_4 + 5\ SO_2 + 2\ H_2O = 2\ KHSO_4 + 2\ MnSO_4 + H_2SO_4.$$

Violet. Colourless (in dilute solution).

In the case of the reduction of potassium chromate by sulphur dioxide there is not enough sulphuric acid produced to convert all the potassium and chromium into sulphates, so

that some free sulphuric acid must be added. Reasoning in a similar manner to that adopted above, the equation representing the reaction is found to be—

$$2\,K_2CrO_4 + 3\,SO_2 + 2\,H_2SO_4 = 2\,K_2SO_4 + Cr_2(SO_4)_3 + 2\,H_2O.$$

Yellow. Green.

QUESTIONS.—CHAPTER VI.

1. What is Avogadro's hypothesis? Indicate the nature of the evidence on which it is based.

2. Define atomic weight; molecular weight. What is the relation of the molecular weight of a gas to its density relative to hydrogen?

3. Explain *fully* what the formulae O_2 and CO_2 represent.

4. State all that is implied by the chemical equation—

$$2\,H_2 + O_2 = 2\,H_2O.$$

CHAPTER VII.

ACIDS. BASES. SALTS. TYPES OF CHEMICAL CHANGE.

45. Acids. History.—The acids known to the early chemists were of vegetable origin, *e.g.* acetic, tartaric, and citric acids. Vinegar, obtained from sour wine, was distilled and a weak solution of acetic acid was obtained, and this was considered the typical acid (Lat. *acidus*, sour or acid). The properties associated with an " acid " by Robert Boyle were—

(1) Sourness.

(2) Solubility in water.

(3) Power of removing the alkaline properties of such substances as caustic soda and caustic potash.

(4) Power of changing the colour of certain blue vegetable substances (such as litmus) to red.

(5) Corrosive action.

(6) Power to precipitate sulphur from alkaline solutions of sulphur.

It was found, however, that certain substances not included under the head of acids possessed all these properties. Thus alum has a sour taste, is soluble in water, deprives caustic soda of its alkaline properties, and turns blue litmus red.

After Lavoisier's discovery that the compounds produced by burning certain elements in oxygen yield acids with water, he assumed that *oxygen was the essential constituent of an acid*. This view was not generally held when it was proved that certain acids such as hydrochloric acid (HCl) and sulphuretted hydrogen (H_2S) do not contain oxygen at all, and that some oxides form alkalies, not acids, with water. A distinction was then made between acids which do contain oxygen and

those which do not. The former were (and still are) called *oxyacids* and the latter *hydracids*.

It was Davy in 1815 who first showed that *hydrogen* and not oxygen is the essential constituent of an acid. He was led to this conclusion by the discovery that iodic anhydride (I_2O_5), which contains oxygen but no hydrogen, is not an acid, but on treating it with water (*i.e.* with a compound of of hydrogen and oxygen) it acquires acid properties. About the same time Dulong arrived at a similar conclusion as a result of studying the action of metallic oxides on oxalic acid. He considered that when an acid was treated with a metallic oxide the metal of the oxide replaced the hydrogen of the acid with formation of a *salt*.

At the present time an acid may be defined as a substance which :—

(1) Contains hydrogen, part or all of which is replaced by a metal when the acid is treated with the metal itself (not in all cases), or with an oxide or hydroxide of the metal;

(2) Usually has a sour taste;

(3) Is usually corrosive;

(4) Changes the colour of certain blue vegetable substances to red, or in certain cases (carbonic acid, boric acid) to a claret colour.

Clause (1) of this definition excludes such substances as alum which fulfil the remaining conditions. A very good and concise definition of an acid is the following :—

An acid is a substance containing hydrogen, part or all of which it exchanges for potassium (or sodium) when brought in contact with caustic potash (or caustic soda).

46. Salts.—A salt may be defined as **a substance produced by the replacement of part or all of the hydrogen of an acid by a metal, or group of elements (such as NH_4) which takes the place of a metal.**

Thus when zinc dissolves in hydrochloric acid the zinc replaces the hydrogen of the acid forming the salt zinc chloride, $ZnCl_2$—

$$\underset{}{Zn} + \underset{\text{Acid.}}{2\,HCl} = \underset{\text{Salt.}}{ZnCl_2} + H_2.$$

Again, when one molecule of caustic soda, NaOH, reacts with one molecule of sulphuric acid, H_2SO_4, part of the hydrogen of the acid is replaced by the metal sodium, forming the salt acid sodium sulphate, $NaHSO_4$—

$$\underset{}{NaOH} + \underset{\text{Acid.}}{H_2SO_4} = \underset{\text{Salt.}}{NaHSO_4} + H_2O.$$

47. Bases.—F. G. Rouelle first used the word **base** to include the earths, alkalies, calces, and all substances which with acids produce salts. A base may be defined as **a substance which with an acid produces a salt and water only.** The substances included as bases, adopting this definition, are basic oxides and hydroxides of the metals, or of a group of elements equivalent to a metal (*e.g.* NH_4). Thus, hydrochloric acid reacts with the base calcium oxide, to produce the salt calcium chloride and water—

$$\underset{\text{Base.}}{CaO} + \underset{\text{Acid.}}{2\,HCl} = \underset{\text{Salt.}}{CaCl_2} + \underset{\text{Water.}}{H_2O}.$$

Again, sulphuric acid reacts with the base zinc hydroxide, to produce the salt zinc sulphate and water—

$$\underset{\text{Base.}}{Zn(OH)_2} + \underset{\text{Acid.}}{H_2SO_4} = \underset{\text{Salt.}}{ZnSO_4} + \underset{\text{Water.}}{2\,H_2O}.$$

Also nitric acid reacts with the base ammonium hydroxide, to produce the salt ammonium nitrate, and water—

$$\underset{\text{Base.}}{NH_4OH} + \underset{\text{Acid.}}{HNO_3} = \underset{\text{Salt.}}{NH_4NO_3} + \underset{\text{Water.}}{H_2O}.$$

Usually, certain substances are, for convenience, called bases which do not conform to the above definition. These are ammonia (NH_3), and its numerous derivatives (such as aniline) which are met with amongst the compounds of carbon. These substances form salts with acids, but without the production of water. Thus ammonia with hydrochloric acid gives the salt ammonium chloride—

$$\underset{}{NH_3} + \underset{\text{Acid.}}{HCl} = \underset{\text{Salt.}}{NH_4Cl}.$$

It is unfortunate that a separate name has not been adopted for these substances.

Alkalies.—Those bases which are soluble in water, such as caustic soda and lime, are called **alkalies** (from the Arabian, *alkali*, ashes of a plant).

48. Basicity of Acids.—Some acids can only produce one salt by interaction with a given base, whereas others can form two, three, or even four different salts.

Thus hydrochloric acid only gives one salt with potash, whereas sulphuric acid gives two salts. On comparing the formulae of these acids—HCl, H_2SO_4—it will be noticed that whilst the former only contains one atom of hydrogen in its molecule the latter has two. When we neutralise hydrochloric acid with caustic potash, we replace the hydrogen atom of each of the molecules of acid by potassium according to the equation—

$$KOH + HCl = KCl + H_2O,$$

and when we only add half the quantity of potash required for neutralisation, we replace the hydrogen atoms of half the HCl molecules by potassium according to the same equation. The other half of the HCl molecules remains unattacked.

On neutralising sulphuric acid with caustic potash, the two hydrogen atoms of each molecule of the acid are replaced by potassium according to the equation—

$$2\,KOH + H_2SO_4 = K_2SO_4 + 2\,H_2O.$$

When, however, only half the quantity of potash is used only one atom of hydrogen in each molecule of the acid is replaced by potassium, the equation being—

$$KOH + H_2SO_4 = KHSO_4 + H_2O.$$

Phosphoric acid contains three atoms of hydrogen, and gives rise to three classes of salts according as one, two, or all of these atoms are replaced by a metal—

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O.$$
$$H_3PO_4 + 2\,NaOH = Na_2HPO_4 + 2\,H_2O.$$
$$H_3PO_4 + 3\,NaOH = Na_3PO_4 + 3\,H_2O.$$

It must not be assumed that all the atoms of hydrogen in an acid are necessarily replaceable by a metal; this is often

not the case. For instance, acetic acid has the formula $C_2H_4O_2$, but only one of the four hydrogen atoms can be replaced by a metal. To indicate this we may write the formula $C_2H_3O_2{\cdot}H$, showing that one hydrogen atom differs in properties from the others. On neutralising acetic acid with caustic soda the following change takes place :—

$$C_2H_3O_2{\cdot}H + NaOH = C_2H_3O_2{\cdot}Na + H_2O.$$

The number of atoms of hydrogen replaceable by a metal contained in one molecule of an acid, is termed the *basicity* of the acid. Thus the basicity of hydrochloric acid is 1, of sulphuric acid 2, of phosphoric acid 3, and of acetic acid 1 ; or, in other words, hydrochloric and acetic acids are *monobasic*, sulphuric acid is *dibasic*, and phosphoric acid is *tribasic*.

49. Normal and Acid Salts.—Salts produced by the replacement of the whole of the replaceable hydrogen of an acid by metals are called *normal salts*. Potassium chloride (KCl), normal potassium sulphate (K_2SO_4), trisodium phosphate, or normal sodium phosphate (Na_3PO_4), and sodium acetate ($C_2H_3O_2{\cdot}Na$) belong to this class. When only part of the replaceable hydrogen of an acid is replaced by metals, the resulting salts are known as *acid salts*. Such are potassium hydrogen sulphate or acid potassium sulphate ($KHSO_4$), disodium hydrogen phosphate (Na_2HPO_4), and sodium dihydrogen phosphate (NaH_2PO_4).

It should be noticed that normal salts are not by any means always *neutral* to litmus and similar indicators. Some of them show an acid reaction (*e.g.* copper sulphate, $CuSO_4$), whilst others show an alkaline reaction (*e.g.* normal sodium carbonate, Na_2CO_3). (See *Inorganic Chemistry, Mainly Metals*). Sodium chloride and normal potassium sulphate are examples of normal salts which are neutral.

So, again, though many acid salts are *acid* to litmus, this is not true for all. Disodium hydrogen phosphate, for instance, shows an *alkaline* reaction.

50. Basic Salts.—On considering the formulae of the bases potassium hydroxide, KOH, lead hydroxide, $Pb(OH)_2$, and bismuth hydroxide, $Bi(OH)_3$, it will be noticed that they

differ in the number of hydroxyl (OH) groups which they contain. The question arises, whether these OH groups can be successively replaced by the acid group of an acid (*e.g.* NO_3, the acid group of nitric acid) in the same way that the hydrogen atoms of a polybasic acid can be successively replaced by a metal. This is found to be the case very frequently, and, just as the basicity of an acid is determined by the number of replaceable hydrogen atoms its molecule contains, so the *acidity* of a base is determined by the number of hydroxyl groups it contains. (We will leave out of consideration for the present the case of *oxides*, dealing only with *hydroxides*.) Thus KOH is a *monacid* base, $Pb(OH)_2$ is a *diacid* base, and $Bi(OH)_3$ is a *triacid* base.

When only part of the OH groups of a base are replaced by an acid group, the salt formed is termed a *basic salt*. Thus $Pb(OH)_2$ gives basic lead nitrate, $Pb(OH)(NO_3)$, by the replacement of one of its hydroxyl groups by the acidic group NO_3 (from HNO_3). When both hydroxyl groups are replaced, normal lead nitrate, $Pb(NO_3)_2$, is formed.

Basic salts may be made in the following three ways :—

(1) By treating the base with insufficient acid to convert the whole of the base into the normal salt. Thus, on treating a molecule of bismuth hydroxide with one of nitric acid, only one of the OH groups of the base is replaced by NO_3—

$$Bi(OH)_3 + HNO_3 = Bi(OH)_2NO_3 + H_2O.$$

(2) By treating the normal salt with excess of water. Here normal bismuth nitrate is converted by the action of water into the same basic salt that was obtained in (1)—

$$Bi(NO_3)_3 + 2\,H_2O = Bi(OH)_2\,NO_3 + 2\,HNO_3.$$

(3) By mixing the normal salt and the free base. On mixing normal lead acetate and lead hydroxide, basic lead acetate is produced—

$$Pb(C_2H_3O_2)_2 + Pb(OH)_2 = 2\,Pb(OH)(C_2H_3O_2).$$

Basic salts can be derived from oxides as well as from hydroxides. One atom of oxygen is equivalent in combining capacity to two hydroxyl (OH) groups. Thus, CaO (quicklime), on treatment with water, forms $Ca(OH)_2$, slaked lime.

Hence a basic oxide having the formula MO, where M is a metal, will be a *diacid* base; for it will be able to neutralise as much acid as a basic hydroxide which contains *two* hydroxyl groups. Thus quicklime, CaO, and slaked lime, $Ca(OH)_2$, both neutralise two molecules of nitric acid—

$$CaO + 2\,HNO_3 = Ca(NO_3)_2 + H_2O.$$
$$Ca(OH)_2 + 2\,HNO_3 = Ca(NO_3)_2 + 2\,H_2O.$$

An example of a basic salt derived from an oxide is bismuth oxychloride, BiOCl. This may be obtained by the action of excess of water on bismuth trichloride—

$$BiCl_3 + H_2O = BiOCl + 2\,HCl.$$

It should be pointed out that all basic salts can be considered as compounds of normal salts with the free base, and in many cases this is the most convenient way of treating them; thus white lead, or basic lead carbonate, is formulated $2\,PbCO_3 + Pb(OH)_2$, basic mercuric sulphate is $HgSO_4 + 2\,HgO$. Reverting to the examples given above, we may write their formulae out again on the plan just mentioned, and show as below that the two sets of formulae are equivalent—

Basic lead nitrate $= Pb(OH)_2 + Pb(NO_3)_2 = Pb_2(OH)_2(NO_3)_2$
$= 2\,Pb(OH)(NO_3).$

Basic bismuth nitrate $= 2\,Bi(OH)_3 + Bi(NO_3)_3 = Bi_3(OH)_6(NO_3)_3$
$= 3\,Bi(OH)_2NO_3.$

Basic lead acetate $= Pb(OH)_2 + Pb(C_2H_3O_2)_2 = Pb_2(OH)_2(C_2H_3O_2)_2$
$= 2\,Pb(OH)(C_2H_3O_2).$

Bismuth oxychloride $= Bi_2O_3 + BiCl_3 = Bi_3O_3Cl_3 = 3\,BiOCl.$

Basic salts are usually less soluble in water than the corresponding normal salts, but there are exceptions.

51. Types of Chemical Change.—In the foregoing chapters we have met with several different kinds of chemical change, and it will be well before going further to classify these under a few main headings.

(1) *Direct Combination.*—This consists in the union of two or more simpler molecules (either elementary or compound) to form a more complex molecule. For example, the two

elements iron and sulphur combine on heating to form ferrous sulphide; the two compounds quicklime and water unite to form slaked lime; and the element chlorine unites with the compound carbon monoxide to form phosgene gas—

$$\underset{\text{Iron.}}{Fe} + \underset{\text{Sulphur.}}{S} = \underset{\text{Ferrous sulphide.}}{FeS}.$$

$$\underset{\text{Quicklime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Slaked lime.}}{CaH_2O_2}.$$

$$\underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Carbon monoxide.}}{CO} = \underset{\text{Phosgene gas.}}{COCl_2}.$$

(2) *Simple Decomposition.*—This term is applied to the breaking up of a complex molecule into simpler molecules (either elementary or compound). For example, mercuric oxide on heating decomposes into mercury and oxygen, chalk on heating breaks up into quicklime and carbon dioxide, and potassium nitrate on heating yields oxygen and potassium nitrite—

$$\underset{\text{Mercuric oxide.}}{2\,HgO} = \underset{\text{Mercury.}}{2\,Hg} + \underset{\text{Oxygen.}}{O_2}.$$

$$\underset{\text{Chalk.}}{CaCO_3} = \underset{\text{Quicklime.}}{CaO} + \underset{\text{Carbon dioxide.}}{CO_2}.$$

$$\underset{\text{Potassium nitrate.}}{2\,KNO_3} = \underset{\text{Potassium nitrite.}}{2\,KNO_2} + \underset{\text{Oxygen.}}{O_2}.$$

(3) *Simple Replacement.*—When an element acts on a compound by replacing another element, the change may be termed "simple replacement." Zinc, for example, acts on sulphuric acid and replaces the hydrogen—

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2}.$$

Similarly, iron reacts with copper sulphate and replaces the copper—

$$\underset{\text{Iron.}}{Fe} + \underset{\text{Copper sulphate.}}{CuSO_4} = \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Copper.}}{Cu}.$$

(4) *Double Decomposition.*—In this kind of change two compounds react and undergo a mutual exchange of con-

stituents. For example, silver nitrate reacts with sodium chloride to produce silver chloride and sodium nitrate—

$$AgNO_3 + NaCl = NaNO_3 + AgCl.$$

Silver nitrate. Sodium choride. Sodium nitrate. Silver chloride.

Again, copper oxide and sulphuric acid (or hydrogen sulphate) react to form copper sulphate and water (or hydrogen oxide)—

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Copper oxide. Sulphuric acid. Copper sulphate. Water.

52. Metals and Non-Metals.—There is little difficulty in recognising the commoner metals by means of their physical properties; they are generally heavy, solid, and opaque, good conductors of heat and electricity, and when freshly scratched or cut exhibit a characteristic lustre. Similarly the common non-metals (*i.e.* the elements which are *not metals*) are easily recognised because their properties are in general the opposite of those just mentioned. Thus iron and silver are unmistakably metals, and phosphorus and oxygen non-metals. But in the case of some elements it is very difficult to say whether they are metals or non-metals; as one element may at the same time exhibit properties belonging to both classes.

From the chemist's point of view, however, an examination of the chemical properties of an element provides a more definite distinction than that of its physical properties. We have seen above that some elements form basic oxides, whilst others give rise to acidic oxides, and that the former property is characteristic of the metals and the latter of the non-metals. This distinguishing chemical property along with others is considered in the following list :—

(*a*) *Characteristic Chemical Properties of Metals:*—

(1) Metals form basic oxides.

(2) Metals usually dissolve in dilute mineral* acids with evolution of hydrogen.†

* *Mineral* acids are acids which are derived from mineral matter, such as hydrochloric and sulphuric acids.

† Nitric acid is usually an exception, as hydrogen is rarely evolved.

(3) Metals either do not combine with hydrogen or form unstable compounds with it.

(*b*) *Characteristic Chemical Properties of Non-Metals :—*

(1) Non-metals form acidic oxides.

(2) Non-metals are not acted upon by dilute mineral acids.

(3) Non-metals usually form stable compounds with hydrogen.

The metals are also distinguished by the fact that when exposed to air or oxygen, especially when heated, they usually lose their brightness of surface and become dull ; the non-metals either undergo no change at all, or are acted upon much less readily.

We have already mentioned that the two classes exhibit distinct *physical* properties, by which they are popularly distinguished.

(*c*) *Characteristic Physical Properties of Metals :—*

(1) They are solids at ordinary temperatures (except mercury).

(2) They reflect light well, especially at a polished or freshly-cut surface ; in short, they possess a pronounced lustre.

(3) They are often capable of being hammered into plates or drawn into wire ; in other words, they are malleable and ductile.

(4) They have usually a high specific gravity.

(5) They are good conductors of heat and electricity.

(6) They are volatilised, as a rule, only at very high temperatures.

(*d*) *Characteristic Physical Properties of Non-Metals :—*

(1) They may be gases, liquids, or solids at ordinary temperatures.

(2) They do not, as a rule, reflect light well.

(3) They are brittle if solid.

(4) They generally have a low specific gravity.

(5) They are usually bad conductors of heat and electricity.

(6) Those which are not gases at ordinary temperatures are transformed into the gaseous condition at comparatively low temperatures, except in three notable cases, viz. carbon, silicon, and boron.

Each of these properties may be exceptionally absent, and must be accepted as only indicating generally the characters of metals when compared with non-metals. It cannot be said that they furnish a means of drawing a sharp line of demarcation between the two classes. Gold and platinum may be precipitated as black powders, though they regain their lustre on being burnished by rubbing with a piece of smooth agate or steel. The non-metals, silicon, boron, iodine, and carbon in the form of diamond and graphite, possess lustre, which differs, however, from the peculiar lustre which can only be described as " metallic."

Again, some metals have quite low specific gravities; lithium, sodium, and potassium, for instance, are lighter than water, and the specific gravities of magnesium and aluminium are only 1·75 and 2·6 respectively, whereas that of platinum is 21·5; on the other hand, diamond has a specific gravity 3·5, *i.e.* it is twice as heavy as magnesium.

Further, carbon in the form of graphite is a good conductor of both heat and electricity. Also the three elements carbon, silicon, and boron are conspicuous from the fact that they are more difficult to volatilise than any of the metals.

There are a few elements which cannot satisfactorily be placed in either class. Thus arsenic and antimony, in their physical properties, resemble the metals, since they have a metallic lustre and are good conductors of heat and electricity; in their chemical properties, however, they resemble the non-metals; for they form acidic oxides and are insoluble in dilute mineral acids. Such elements are called *metalloids*.

Hydrogen, again, is another element which is difficult to classify. Its physical properties (except the fact that it conducts heat) and some of its chemical properties place it amongst the non-metals; but, since metals will displace hydrogen from acids and will also displace other metals from their salts, hydrogen might be considered to be a metal. It is best to put it with the metalloids.

QUESTIONS.—CHAPTER VII.

1. Write a short history of the term *acid*.

2. Define the terms *acid*, *salt*, *base*, and *alkali*, and give examples of each class of compounds.

3. What is meant by the *basicity* of an acid? Illustrate your answer by examples.

4. Describe an experiment which proves that sulphuric acid is a dibasic acid.

5. What is the basicity of the following acids :—(1) acetic, (2) phosphoric, (3) hydrochloric?

6. Explain the terms *normal salt* and *acid salt*, and give examples of each class of compounds.

7. What is a *basic salt?* By what methods can basic salts be prepared?

8. State the principal types of chemical change, and give examples of each.

9. Into what two classes may elements be divided. What are the characteristic properties of each class?

10. What are *metalloids*? Illustrate your answer by discussing examples.

11. State fully how you would proceed to investigate whether a given solid substance was a metal or a non-metal.

CHAPTER VIII.

ELECTROLYSIS.

53. Electrolysis or Decomposition by the Electric Current.—The electric current was used by Nicholson and Carlisle in 1802 to decompose water, and the process is known as *electrolysis*. Davy obtained sodium and potassium in 1807 by electrolysis of the fused hydroxides. Berzelius, who advanced an electrical theory of chemical compounds, also showed that aqueous solutions of acids, bases, and metallic salts were decomposed by a current of electricity. Berzelius said that all atoms were polarised, and combination took place between oppositely charged atoms or particles, *e.g.*—

$$\overset{+-}{\underset{\text{(pre-eminently positive).}}{Na}} + \overset{-+}{\underset{\text{(pre-eminently negative).}}{Cl}} = NaCl$$

also

$$\overset{+-}{\underset{\text{(Mainly +).}}{K_2O}} + \overset{+-}{\underset{\text{(Mainly -)}}{SO_3}} = K_2SO_4$$

He then suggested that electrolysis was the reverse of salt formation. It was Faraday who, in 1834, studied the phenomena of electrolysis on a quantitative basis.

54. The Electrolysis of Copper Sulphate : Explanation of Electrolysis.—In the following explanations some knowledge of the elements of electricity is assumed.

Fig. 11*a* represents diagrammatically a simple experiment to illustrate electrolysis. PQQ'P' is a vessel containing a solution (in water) of copper sulphate. Immersed in the liquid are two platinum plates, A*h* and K*l*. These plates are connected by wires to the two poles of an electric battery

LH—a Grove battery of two or three cells answers admirably. The "current" is assumed to flow in the direction represented by the arrows, viz. from H (the positive or copper pole of the battery) to A, down the plate A*h*, through the liquid, up the plate K*l*, from K to L (the negative or zinc pole of the battery), and back to H through the battery.

During the passage of the current chemical action takes place in the copper sulphate solution. Copper is deposited as a thin layer on the plate K*l*, a gas is liberated at the plate A*h* (which can be collected and shown to be oxygen), and sulphuric acid gradually accumulates in the liquid.

Such an action—the decomposition of a liquid by an electric current—is, as already indicated, called *electrolysis*, and the liquid is called the *electrolyte*. The vessel PQQ'P' is called the *electrolytic cell*. The two plates A*h* and K*l* are called the electrodes. The plate A*h*, by which the current enters the cell, is called the *anode*, or the *positive electrode*. The plate K*l*, by which the current leaves the cell, is called the *kathode*, or the *negative electrode*. Note that the positive electrode is coupled with the positive pole of the battery, and the negative electrode with the negative pole.

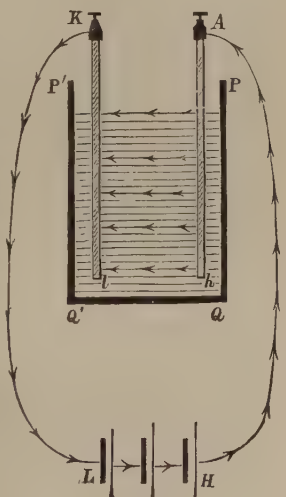


Fig. 11*a*.

The following explanation of the phenomenon just described is at present generally accepted.

It is supposed that when copper sulphate ($CuSO_4$) is dissolved in water, some (in dilute solution the greater part) of the molecules are dissociated into two "ions." The one ion is the atom Cu, and the other is the group of atoms SO_4, which is called *sulphion*. The ion Cu is supposed to carry two *positive* charges of electricity and the ion SO_4 two *negative* charges. When the electrodes are introduced into the

liquids they attract the charged ions; the negative electrode attracts the positively charged ions, *i.e.* the copper ions, and the positive electrode attracts the negatively charged ions, *i.e.* the sulphions. This is in accordance with the ordinary law of electric attraction. There is consequently a stream of Cu ions proceeding towards the negative electrode, and a stream of SO_4 ions proceeding towards the positive electrode. This is represented diagrammatically in Fig. 11*b*, in which $\overset{+}{Cu}$ stands for a positively charged copper ion, and $\overset{-}{SO_4}$ stands for a negatively charged sulphion.

When a Cu ion reaches the negative electrode it gives up its electric charge, and is deposited on the electrode as a thin film. At the same time an SO_4 ion reaches the positive electrode and gives up its charge. An uncharged sulphion is, however, incapable of a separate existence, and immediately reacts with the water in contact with the positive electrode, with formation of sulphuric acid and liberation of oxygen.

$$2\,SO_4 + 2\,H_2O = 2\,H_2SO_4 + O_2.$$

The ion Cu, which is attracted to the kathode, is called the *kathion*; and the ion SO_4, which is attracted to the anode, is called the *anion*.

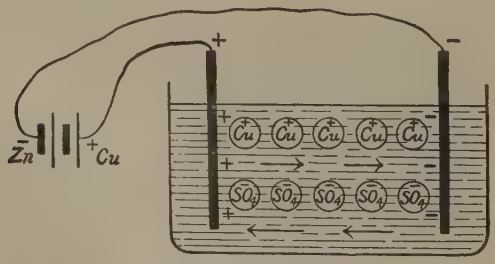


Fig. 11*b*.

55. Electrolysis in General.—This process of electrolysis is very general in its application. All acids, alkalies, and salts in the liquid state are electrolytes (whether naturally liquid or liquefied by heat or solution); that is to say, they will be

decomposed by an electric current. In the case of salts, the kathion always consists of the atom or atoms of metal in the molecule, the remainder of the molecule forming the anion. In the case of acids, the kathion consists of the atom or atoms of hydrogen in the molecule.

The properties of these ions are different from those of the substances as we ordinarily know them; *e.g.* ionic sodium does not decompose water. But when the ions reach the electrodes their charge is neutralised, and they resume their normal chemical properties. Hence it frequently happens that further chemical action takes place at one or both electrodes between the discharged ions and the liquid or the metal of which the electrodes are composed.

56. Electrolysis of Water.—Pure water does not conduct electricity, but when an acid, base, or salt is dissolved in it, it becomes an electrolyte. Thus water acidulated with sulphuric acid is decomposed by the electric current.

The part played by the sulphuric acid is explained as follows :—The acid on solution dissociates into three ions, two of hydrogen (H) and one of sulphion (SO_4). The H ions carry positive charges of electricity and the SO_4 ion negative charges. On passing the current, the H ions are attracted to the negative electrode, where they give up their charge and acquire the properties which we ordinarily associate with hydrogen. One of these is that free atoms of hydrogen cannot exist separately; they therefore combine to form molecules, in which form the gas passes off and may be collected. The sulphions are attracted to the positive electrode, and after giving up their charges undergo a secondary reaction with water with liberation of oxygen, as already described in the previous paragraph.

Let us start with, say, two* molecules of sulphuric acid, and trace the changes which they undergo. We may represent the primary change on passing the current by the equations—

$$2\,H_2SO_4 \rightleftharpoons 4\,H^{\cdot} + 2\,SO_4''.$$
$$4\,H = 2\,H_2.$$

* *Two* molecules are used instead of one to avoid writing an *atom* of oxygen in the second equation.

The $2\,H_2$ is evolved at the kathode and the $2\,SO_4$ liberated at the anode reacts with water thus—

$$2\,SO_4 + 2\,H_2O = 2\,H_2SO_4 + O_2.$$

The O_2 is evolved at the anode.

We therefore finish with the same amount of sulphuric acid with which we started, *i.e.* 2 molecules, and the net result of passing the current has been to break up two molecules of water into two molecules of hydrogen and one molecule of oxygen. The same result would have been arrived at if we had taken any other number of sulphuric acid molecules, from which it follows that the amount of sulphuric acid in the cell remains unchanged, and the gases ultimately liberated are the constituents of pure water.

57. Electrolysis of Hydrochloric Acid.—If strong hydrochloric acid be substituted for dilute sulphuric acid the ions are hydrogen and chlorine. On passing the current, hydrogen at once appears at the kathode, but no chlorine makes its appearance, for two reasons: firstly, because chlorine is soluble in the acid solution; and, secondly, because the chlorine, while still in the condition of free atoms (*nascent* chlorine), attacks the platinum anode, converting it into the soluble platinum chloride ($PtCl_4$).

If the anode be a plate of gas carbon, on which chlorine, even when nascent, has no action, and if the solution be saturated with chlorine beforehand, hydrogen and chlorine appear in equal volumes.

58. Electrolysis of Solutions of Alkalies.—When caustic soda (NaOH) dissolves in water it separates into the two ions, sodium and hydroxyl (OH). On passing a current through the solution, the former is liberated at the kathode and the latter at the anode. Neither of these, however, appears, because of secondary actions, the sodium immediately decomposing water with evolution of hydrogen and re-formation of caustic soda, and the hydroxyl breaking up into oxygen, which escapes, and water, which remains.

Considering the changes which four* molecules of NaOH undergo we have as the primary change on passing the current—

$$4\ NaOH \rightleftharpoons 4\ Na^{\cdot} + 4\ OH'.$$

The following secondary changes then take place. At the kathode—

$$4\ Na + 4\ H_2O = 4\ NaOH + 2\ H_2.$$

At the anode—

$$4\ OH = 2\ H_2O + O_2.$$

The net result is that the amount of caustic soda remains unchanged and water is decomposed into hydrogen and oxygen. It will, therefore, be seen that the electrolysis of dilute sulphuric acid and of caustic soda solution both bring about the same result, namely, the decomposition of water.

59. Electrolysis of Solutions of Salts.—Here the immediate products of the decomposition (ions) are the metal and the acid radicle—SO_4, Cl, NO_3, etc.—the former, like the metal of an alkali and the hydrogen of an acid, always going to the kathode, and the latter always going to the anode when the current is passed.

But whether these ions actually appear or not after giving up their charges to the electrodes, depends upon the nature of the ions and the presence or absence of secondary actions between them and the liquid or the electrodes. Except in the case of those metals which decompose water at the ordinary temperature (Na, K, and a few others), the metal is always deposited on the kathode; but, except in the case of some of the hydracids (HCl, HI, etc.), the acid radicle rarely appears as such, even if no action takes place between it and the anode. In the case of sulphates, as we have seen, the acid radicle SO_4 reacts with water forming sulphuric acid, with liberation of oxygen. In the case of nitrates the radicle NO_3 behaves in a similar manner, yielding nitric acid and liberating oxygen—

$$4\ NO_3 + 2\ H_2O = 4\ HNO_3 + O_2.$$

* Four molecules are used for a similar reason to that referred to in the footnote on p. 81.

If a solution of zinc sulphate ($ZnSO_4$) be electrolysed between platinum electrodes, zinc is deposited on the kathode, and for every atom of zinc deposited an atom of oxygen is liberated at the anode and a molecule of sulphuric acid goes into solution. But if a plate of zinc replaces the platinum anode, the SO_4 group, instead of reacting with water, simply combines with the zinc to form $ZnSO_4$. Then for every molecule of $ZnSO_4$ decomposed, and for every atom of zinc deposited at the kathode, an atom of zinc is dissolved and a molecule of zinc sulphate re-formed at the anode; so that the kathode gains exactly as much zinc as the anode loses, and the average composition of the solution remains unaltered.

With copper sulphate ($CuSO_4$) electrolysed between copper electrodes the action is less simple. Copper is deposited on the kathode, but at the anode some of the SO_4 directly unites with the copper to re-form copper sulphate, and some reacts with water forming sulphuric acid, with liberation of oxygen. Part of this oxygen escapes, while some unites with the copper to form copper oxide (CuO), which in part incrusts the plate, and in part dissolves in the acid to re-form copper sulphate— $CuO + H_2SO_4 = CuSO_4 + H_2O$.

60. Electro-chemical Equivalents. Faraday's Laws.—If the same current be passed successively through several electrolytic cells containing solutions of salts of different metals, *all these metals will be deposited in amounts proportional to their chemical equivalents.*

Take three electrolytic cells containing respectively (*a*) acidulated water, (*b*) a solution of silver nitrate, (*c*) a solution of copper sulphate. Connect them in series with a battery so that the whole current passes through each cell in succession. Find the weight of hydrogen liberated in (*a*), of silver deposited in (*b*), and of copper deposited in (*c*). Suppose these weights are respectively 0·01038 grm., 1·112 grm., and 0·3281 grm.

We can now determine the weight of silver and of copper deposited for each gramme of hydrogen liberated. Thus—

$1{\cdot}112 \div 0{\cdot}01038 = 107{\cdot}1$ for silver.

$0{\cdot}3275 \div 0{\cdot}01038 = 31{\cdot}55$ for copper.

Such numbers may be termed the **Electro-chemical Equivalents.** A more complete list is given in the following table, together with the atomic weights :—

TABLE OF ELECTRO-CHEMICAL EQUIVALENTS, TOGETHER WITH ATOMIC WEIGHTS.

Metal.	E.C. Equivalent.	Atomic Weight.
Gold	65·7	197·2
Silver	107·88	107·88
Copper	31·8	63·57
Mercury	100·3 and 200·6	200·6
Tin	29·6 and 59·3	118·7
Iron	18·6 and 27·92	55·84
Zinc	32·68	65·37
Lead	103·6	207·2

A consideration of the preceding shows—

(1) That *chemically* equivalent quantities of the elements are set free by the passage of the same quantity of electricity.

(2) That the *electro-chemical* equivalent is either equal to the atomic weight or a simple submultiple of it; (*i.e.* the electro-chemical equivalent $= \left(\frac{\text{atomic weight}}{\text{valency}}\right)$.

(3) That in some cases the same element gives more than one value. In these cases the values are found to correspond with the equivalent of the element in the particular compound electrolysed.

It was also found by Faraday, by whom these relationships were discovered, that the amount of an element deposited bears a definite proportion to the amount of electricity passed. These facts are embodied in what are known as **Faraday's Laws of Electrolysis** :—

(1) The quantities of the elements deposited in the same circuit are chemically equivalent.

(2) The quantities deposited are proportional to the quantity of electricity passed (current $\times$ time).

As the chemical and the electro-chemical equivalents are numerically equal, it can readily be seen that each univalent atom carries the same amount of electricity. This unit

charge of the ion, as it is called, is 96,540 coulombs.* A bivalent ion then carries two charges or 193,080 coulombs.

61. Useful Applications. Electro-deposition.—The principle of electrolysis has many useful applications in the arts. One of the oldest of these is the process of *electroplating*. Here the object to be plated is thoroughly cleaned and slightly roughened, and made the kathode of an electrolytic cell, the anode being a plate of the metal to be deposited, and the electrolyte a solution of a salt of that metal, the current being supplied by a battery or dynamo. A thin and firmly adherent film of the metal—gold, silver, nickel, or what not—is deposited on the article to be plated, and the strength of the solution is kept up by the action of the electrolyte on the anode. Compare with this the above description of the electrolysis of zinc sulphate, when a zinc anode is used.

A very important electroplating industry is electro-*silvering*. In this case the salt is a double cyanide of silver and potassium, the " bath " being prepared by dissolving one part (by weight) of silver cyanide and two of potassium cyanide in forty of distilled water. The current is maintained until the deposit amounts to about one ounce per square foot, which corresponds to a thickness of about $\frac{1}{800}$ in.

Electro-*gilding* is the art of coating objects with gold. The bath is a solution of the double cyanide of gold and potassium. The details are similar to those for electro-silvering, except that the current employed is weaker and the deposit thinner.

Electro-*nickeling* is the art of coating objects (usually of steel, such as the handle-bars of bicycles) with nickel. The bath is a slightly acid solution of the double sulphate of nickel and ammonium. A good coat consists of about $\frac{2}{3}$ oz. per sq. ft., which represents about $\frac{1}{1000}$ in. in thickness.

Electro-*coppering* is the easiest of all the plating processes. The bath is simply a strong and very slightly acid solution of copper sulphate. When *iron* is the metal to be coppered the simple copper sulphate bath is unsuitable, because the sulphate would be rapidly decomposed by the iron; in this case the

* The coulomb is the unit of quantity of electricity, and equals one ampere-second.

bath consists of an alkaline solution of the double tartrate of copper and sodium obtained by adding excess of sodium hydroxide to a solution of copper sulphate and tartaric acid.

In *electrotyping*, the object is to produce not a thin adherent coat, but a thick one, which may be readily detached from the mould which serves as the kathode, and which reproduces, with the utmost fidelity, all the form and relief of the original article. Engraved wood blocks, for instance, are thus reproduced in copper. A mould is first prepared in gutta-percha, plaster of Paris, or some other substance. The face of this mould is then black-leaded to form a conducting film, and the mould is hung in a solution of sulphate of copper, in which it becomes the kathode, the anode being a sheet of copper suspended in the solution. When the deposited copper forms a layer of sufficient thickness it is removed from the mould, backed with type metal, and mounted type-high on a wood block.

62. Electrometallurgy.—Many metals are now economically extracted from their compounds by electrolysis—sodium, for instance, the electrolyte being caustic soda melted by heat. Sodium and hydrogen separate at the kathode, the latter being allowed to escape, and oxygen at the anode. Aluminium is similarly obtained by the electrolysis of alumina dissolved in a bath of molten fluorides of aluminium, sodium, and calcium. Many other examples will be observed by the student as this volume and *Inorganic Chemistry, Mainly Metals* are read.

63. Fractional Electrolysis.—Magnus in 1856 found that when a solution of salts of different metals is electrolysed, there is a certain definite voltage at which one and only one of the metals is deposited. In other words, it may be said that a certain voltage, called the *decomposition voltage*, is required to electrolyse a given solution, *e.g.* hydrochloric acid requires 1·25 volts, nickel sulphate requires 1·95 volts, before nickel is deposited. Thus in a mixed solution of nickel and copper sulphate, copper alone is deposited when the voltage reaches 1·29 volts, and the nickel remains in solution until 1·95 volts is reached.

This phenomenon is the basis of many methods of analysis and of industrial processes. Thus crude copper is refined by using it as an anode in a bath of a solution of acidified copper sulphate. The cathode consists of sheets of pure copper, and the current is regulated so that only copper is deposited on the cathode, the impurities of the anode passing into solution.

In these cases of *fractional electrolysis* the size of the cathode, and the concentration of the solution are important. The larger the cathode the lower is the electromotive force required for the deposition of the pure metal. The *current density* is the number of amperes per unit surface at the cathode, and unit surface is usually taken to be the square decimetre. Thus the current density is the most important factor in electrolysis, as it determines the character and the nature of the products obtained.

QUESTIONS.—CHAPTER VIII.

1. Describe what you would observe when a current of electricity is passed through aqueous solutions of the following substances, using platinum electrodes :—(1) copper sulphate ; (2) sulphuric acid ; (3) caustic potash.

2. Explain the meaning of the terms—*electrolysis, ion, anode, kathode.*

3. What do you understand by an *electrolyte* ? Describe and explain as far as you can what takes place when an electric current is passed through (i) a solution of caustic soda, (ii) fused caustic soda.

4. Give an account of three different cases of preparing chemical elements by electrolysis, with the precautions to be taken for collecting the products.

5. Describe and explain what takes place when a current of electricity is passed through a solution of zinc sulphate between platinum electrodes.

6. The same electric current is passed through solutions of copper sulphate and stannic chloride. What will be the relationship between the weights of metals deposited, and what law do they illustrate ?

7. Give Faraday's Laws of Electrolysis, and explain how you would prove them.

8. Describe a method of determining the *electro-chemical equivalent* of copper. Explain the meaning of the term.

9. Write a short account of the applications of the principle of electrolysis which have been made in the arts.

10. Explain the meaning of the term " fractional electrolysis." Give examples of the use of fractional electrolysis in industry.

CHAPTER IX.

MODES OF FORMATION OF SALTS.

64. Definition of the Term "Salt."—In Chapter VII. we defined a salt as a substance produced by replacing the hydrogen of an acid by a metal. We may now, in the light of the electrolytic theory discussed in the previous chapter, give another definition, viz. **a salt is a substance which when dissolved in water breaks up more or less completely into two types of ions, one of which is a metal or group of elements equivalent to a metal** (*e.g.* NH_4), **and the other a non-metal or a non-metallic radicle** (*e.g.* SO_4). This definition includes both acids and bases,* as well as the substances which are usually termed salts, for in a solution of an acid the hydrogen acts as a metallic ion, and in a solution of a base the hydroxyl radicle constitutes the non-metallic ion. An example will illustrate the relation between the three classes of bodies—

	Metallic ion.	Non-metallic ion.
Nitric acid	$\overset{+}{H}$	$\overset{-}{NO_3}$
Caustic potash	$\overset{+}{K}$	$\overset{-}{OH}$
Potassium nitrate ...	$\overset{+}{K}$	$\overset{-}{NO_3}$

65. Modes of Formation of Salts.—The various ways in which salts are formed may be summarised as follows :—

* *Oxides* are, of course, not included. Some chemists, however, restrict the term *base* to metallic *hydroxides*.

METHOD 1. DIRECT UNION OF A METAL AND A NON-METAL.—This method is largely employed for the production of the anhydrous salts of the halogen acids, since most metals unite directly with the halogens. When the metal forms two salts, one containing a higher percentage of halogen than the other, it depends upon the relative masses of the metal and the halogen which react, whether the higher or the lower salt is formed. Iron, for instance, yields ferr*ic* chloride ($FeCl_3$) with excess of chlorine; but if the iron is in excess, ferr*ous* chloride ($FeCl_2$) is formed—

$$2\,Fe + 3\,Cl_2 = 2\,FeCl_3.$$
$$Fe + Cl_2 = FeCl_2.$$

Similarly, tin yields stannic chloride ($SnCl_4$) or stannous chloride ($SnCl_2$), according as chlorine or the metal is in excess—

$$Sn + 2\,Cl_2 = SnCl_4.$$
$$Sn + Cl_2 = SnCl_2.$$

The combination of mercury and iodine affords another example, HgI_2 or Hg_2I_2 being formed according as iodine or mercury is in excess.

Many sulphides can also be readily obtained by the direct union of metals with sulphur (see § 14).

METHOD 2. INTERACTION OF METALS AND ACIDS.—When acids act on metals, a salt of the metal is almost invariably obtained as one of the products. In some cases, *e.g.* when dilute hydrochloric, dilute sulphuric, or acetic acid acts on magnesium, zinc, or iron, hydrogen is the only other product, and these reactions are used in the preparation of hydrogen, as we have seen. In other cases the reactions are more complex, and these are fully discussed in §§ 259, 328.

The action of a haloid acid on a metal always results in the formation of its *lower* salt when it forms more than one. Thus, with hydrochloric acid, iron forms ferrous chloride, $FeCl_2$, and with tin it forms stannous chloride, $SnCl_2$. We should expect this because the nascent hydrogen which is liberated in the reaction is a strong reducing agent, and would immediately reduce the higher salt if any were formed.

When the acid is a strong oxidising agent, *e.g.* nitric acid, the nascent hydrogen which may be supposed to be liberated at first is immediately oxidised to water, and it depends upon the relative masses of the metal and the acid whether the lower or the higher salt is formed. This may be illustrated by the following experiments.

Exp. 19. Warm a small quantity of mercury with excess of nitric acid till the metal has dissolved. Now add hydrochloric acid to the solution; no precipitate will be formed, proving the absence of any mercu*rous* nitrate (which with hydrochloric acid would form a white precipitate of mercurous chloride). The mercury has been entirely converted into mercuric nitrate.

Exp. 20. Next allow some mercury to remain in contact with about half its volume of dilute nitric acid for some time. Pour off the supernatant liquid from the mercury and add hydrochloric acid; a white precipitate is at once formed, showing that when the mercury is in excess of the acid, it is converted into mercu*rous* nitrate.

Salts of the haloid acids may be obtained by acting on a metal with either the gaseous acid or its aqueous solution; if the anhydrous salt is required, only the former method can be employed in many cases, because, on evaporating the aqueous solution of the salt to dryness to drive off water, the salt undergoes decomposition. Aluminium chloride, for instance, is decomposed by water on evaporation to dryness, with formation of aluminium hydroxide, $Al(OH)_3$, and hydrochloric acid—

$$2\ AlCl_3 + 6\ H_2O = 2\ Al(OH)_3 + 6\ HCl.$$

Exp. 21. Dissolve some aluminium in hydrochloric acid and evaporate the solution to dryness in a porcelain dish on a sand-bath. Try to dissolve the white residue in water; it is insoluble (whereas aluminium chloride is soluble) and consists of aluminium hydroxide formed according to the equation given above.

Method 3. Interaction of a Metal with a Salt of Another Metal.—In general one metal will displace another from its salts when the oxide of the former is more strongly basic than that of the latter, *i.e.* the oxide reacts more readily with acids. Thus iron displaces copper from a solution of

copper sulphate (see Exp. 1), and zinc displaces silver from a solution of silver nitrate—

$$Fe + CuSO_4 = Cu + FeSO_4.$$
$$Zn + 2\,AgNO_3 = 2\,Ag + Zn(NO_3)_2.$$

Method 4. Direct Union of a Basic Oxide and an Acidic Oxide.—Many basic oxides combine directly with acidic oxides to form salts. For example, when barium oxide, BaO, and sulphur trioxide, SO_3, are mixed together they combine to form barium sulphate with such energy that the mass becomes red-hot—

$$BaO + SO_3 = BaSO_4.$$

Again, quicklime and carbon dioxide readily unite to form calcium carbonate—

$$CaO + CO_2 = CaCO_3.$$

Adopting the broad definition of a salt which follows, as shown above, from the electrolytic dissociation theory, we may include the formation of acids from acidic oxides and water, and bases from basic oxides and water under this heading; in the formation of acids in this way water plays the part of a basic oxide, and in the formation of bases that of an acidic oxide. Thus, just as barium oxide combines with sulphur trioxide to form barium sulphate, so it combines with water to form the base barium hydroxide, $Ba(OH)_2$; and just as sulphur trioxide combines with barium oxide to form barium sulphate, so it combines with water to form hydrogen sulphate or sulphuric acid.

$$\underset{\text{Basic oxide.}}{BaO} + \underset{\text{Acidic oxide.}}{SO_3} = \underset{\text{Salt.}}{BaSO_4}.$$

$$\underset{\text{Basic Oxide.}}{BaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Base.}}{Ba(OH)_2}.$$

$$\underset{\text{Water.}}{H_2O} + \underset{\text{Acidic oxide.}}{SO_3} = \underset{\text{Acid.}}{H_2SO_4}.$$

Method 5. Interaction of Bases and Acids.—This is the most general method. It is fully discussed in § 47.

METHOD 6. INTERACTION OF AN ACID WITH A SALT OF A MORE VOLATILE ACID.—An example of this method is the conversion of a nitrate into a sulphate by heating with strong sulphuric acid. The volatile nitric acid is driven off, leaving the salt of the much less volatile sulphuric acid behind. Zinc nitrate, $Zn(NO_3)_2$, may in this manner be converted into zinc sulphate, $ZnSO_4$—

$$Zn(NO_3)_2 + H_2SO_4 = ZnSO_4 + 2\,HNO_3.$$

METHOD 7. INTERACTION OF A BASE WITH A SALT OF A MORE VOLATILE BASE.—When caustic potash or soda is heated with an ammonium salt, the volatile base, ammonia, is driven off and the corresponding potassium salt remains—

$$2\,KOH + (NH_4)_2SO_4 = K_2SO_4 + 2\,NH_3 + 2\,H_2O.$$

METHOD 8. INTERACTION OF A BASE WITH A SALT OF AN INSOLUBLE BASE.—The majority of the hydroxides of the metals are insoluble in water. If, then, a solution of a soluble base such as caustic potash or soda is added to a salt of a metal which forms an insoluble hydroxide, double decomposition takes place with precipitation of the insoluble hydroxide and formation of a salt of potassium or sodium; for it is observed that, *when an insoluble substance can be formed by double decomposition, that substance is usually formed.*

For example, on adding caustic potash to a solution of copper sulphate, $CuSO_4$, cupric hydroxide, $Cu(OH)_2$, is precipitated, and potassium sulphate, K_2SO_4, goes into solution—

$$2\,KOH + CuSO_4 = Cu(OH)_2 + K_2SO_4.$$

The potassium sulphate can be separated from the hydroxide by filtration.

METHOD 9. INTERACTION OF TWO SALTS.—Representing the double decomposition between two salts by the equation—

$$A + B = C + D,$$

this method of preparation can be used for a salt, C, when that salt is less soluble or more volatile than A, B, or D. For example, silver chloride, AgCl, is insoluble in water,

whereas silver nitrate, $AgNO_3$, potassium chloride, KCl, and potassium nitrate, KNO_3, are all soluble. We can therefore prepare silver chloride by mixing solutions of silver nitrate and potassium chloride; silver chloride is precipitated and may be separated from the soluble salts by filtration—

$$AgNO_3 + KCl = AgCl + KNO_3.$$

Again, mercuric chloride, $HgCl_2$, is volatile, whilst sodium chloride, sodium sulphate, Na_2SO_4, and mercuric sulphate, $HgSO_4$, are non-volatile. If, therefore, a mixture of mercuric sulphate and sodium chloride is heated together, double decomposition takes place and mercuric chloride passes away as vapour, condensing again on a cool surface.

$$HgSO_4 + 2\,NaCl = HgCl_2 + Na_2SO_4.$$

Method 10. Interaction of Two Bases.—A few bases, notably the oxides and hydroxides of zinc, lead, and aluminium, are soluble in caustic potash or caustic soda solution with formation of salts. The explanation is that, in the presence of a strong base such as caustic potash, a substance which generally acts as a weak base may act as a weak acid. The following equations represent the formation of salts in this manner :—

$$2\,KOH + Zn(OH)_2 = \underset{\text{Potassium zincate.}}{K_2ZnO_2} + 2\,H_2O.$$

$$2\,NaOH + Al_2O_3{\cdot}3H_2O = \underset{\text{Sodium aluminate}}{2\,NaAlO_2.} + 4\,H_2O.$$

$$2\,KOH + PbO = \underset{\text{Potassium plumbite.}}{K_2PbO_2} + H_2O.$$

Method 11. Interaction of Metals with Bases.—A few metals also are soluble in potash solution with evolution of hydrogen, more especially zinc and aluminium. The salts obtained are the same as those produced when the oxides or hydroxides of the metals are used instead of the metals themselves, as in the preceding method : thus when aluminium is dissolved potassium aluminate is formed—

$$2\,KOH + 2\,H_2O + 2\,Al = \underset{\text{Potassium aluminate.}}{2\,KAlO_2} + 3\,H_2.$$

Most metals are attacked slowly by fused potash, silver being the most resistant.

66. Double Salts.—These are salts formed by the union of two simple salts, *e.g.* a molecule of potassium sulphate, K_2SO_4, and one of aluminium sulphate, $Al_2(SO_4)_3$, together with 24 molecules of water, unite together to form a molecule of potassium aluminium sulphate or alum, $K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O$.

Double salts break up on solution into the simple salts of which they are composed, and these then decompose further into ions in the usual way; thus alum breaks up into K_2SO_4 and $Al_2(SO_4)_3$, and these salts then yield the ions K, Al, and SO_4.

67. Complex Salts.—These are salts of complex acids. They do not decompose in the same way as double salts, but ionise immediately, yielding a complex anion containing one of the metals; for example, potassium chloride, KCl, unites with platinum chloride, $PtCl_4$, to form the double salt $2\ KCl + PtCl_4$ or K_2PtCl_6; on dissolving this salt in water the kathions consist of K and the anions of the complex group $PtCl_6$. This salt may, therefore, be considered to be derived from the acid H_2PtCl_6, chloroplatinic acid, and is called potassium chloroplatinate.

Other examples of double salts are carnallite, $KCl + MgCl_2 + 6\ H_2O$, and ferrous ammonium sulphate, $(NH_4)_2SO_4 + FeSO_4 + 6\ H_2O$, and of the complex class, potassium ferrocyanide, $K_4Fe(CN)_6$, which yields the complex anion $[Fe(CN)_6]$.

QUESTIONS.—CHAPTER IX.

1. How is a *salt* defined in terms of the electrolytic theory?

2. Discuss the effect of mass on the nature of the products obtained by the action on metals of (1) the halogens, (2) nitric acid.

3. Why would you expect to get only the *lower* salt when a haloid acid acts on a metal which can give rise to two series of salts?

4. Why cannot anhydrous aluminium chloride be obtained by evaporating the aqueous solution of the salt to dryness? How is the anhydrous salt obtained?

5. Express by equations the action of (1) barium monoxide on sulphur trioxide, (2) zinc on silver nitrate, (3) caustic potash on ammonium sulphate, (4) caustic soda on zinc hydroxide.

6. Under what conditions can a salt be conveniently prepared by the interaction of two other salts ?

7. Give examples of the formation of salts from (1) two bases, (2) a metal and a base.

8. What are double salts and complex salts ? Illustrate your answer by examples.

CHAPTER X.

CHEMICAL CALCULATIONS.

68. The Relations between Weight and Volume of Gases.—From Avogadro's hypothesis it follows at once that *the densities of gases are proportional to their molecular weights.* In order to express the weight of any gas it is convenient to remember as the basis of calculation that 1 *litre of hydrogen at the standard temperature* (0° *C.*) *and pressure* (760 *mm. of mercury*) *weighs* 0·09 *grm.*, or that 11·11 litres of hydrogen weigh one gramme.*

If then we desire to ascertain the weight of any other gas under like conditions, we commence by expressing in chemical symbols the molecule of the gas thus—

The molecule of hydrogen	is expressed by			H_2	(2)
,,	,,	nitrogen	,,	N_2	(28)
,,	,,	oxygen	,,	O_2	(32)
,,	,,	chlorine	,,	Cl_2	(71)
,,	,,	ozone	,,	O_3	(48)
,,	,,	phosphorus	,,	P_4	(124)
,,	,,	water vapour	,,	H_2O	(18)
,,	,,	hydrochloric acid	,,	HCl	(36·5)
,,	,,	carbon dioxide	,,	CO_2	(44)
,,	,,	nitric oxide	,,	NO	(30)
,,	,,	sulphur dioxide	,,	SO_2	(64)
,,	,,	sulphuretted hydrogen	,,	H_2S	(34)
,,	,,	ammonia	,,	NH_3	(17)

and so on.

Then the relative weights are those stated in parenthesis after the symbol in the above list, as derived from the respec-

* Approximate atomic weights are used in this Chapter.

tive atomic weights. Thus the weight of a litre of nitrogen is 14 times that of a litre of hydrogen or (0·09 × 14) grm; a litre of carbon dioxide weighs (0·09 × 22) grm.; a litre of sulphuretted hydrogen weighs (0·09 × 17) grm.

The alternative method of expressing the same facts is perhaps more readily applied in chemical calculations, viz. that 11·11 litres of hydrogen weigh 1 grm. or 22·22 litres of hydrogen weigh 2 grm., the same number of grammes as that used for expressing the molecular weight. In this form the statement is quite general, that the molecular weight being m, 22·22 litres of any gas whatever weigh m grm.

22·22 litres	of	nitrogen	weigh	28 grm.
22·22 ,,	,,	oxygen	,,	32 ,,
22·22 ,,	,,	chlorine	,,	71 ,,
22·22 ,,	,,	sulphur dioxide	,,	64 ,,
22·22 ,,	,,	ammonia	,,	17 ,,

It is convenient to remember both forms of the expression, as one or the other is more readily adapted for the purpose of calculation according to the terms which are given.

For instance, if it be desired to calculate the weight of a certain volume of a gas, the former expression lends itself more readily for the purpose—as in the following example :—

Example 1.—*Required the weight of* 100 *c.cm. of carbon dioxide at* 0° *C. and* 760 *mm. pressure.*

1000 c.cm. (1 litre)	of	hydrogen	weigh	0·09 grm.
,,	,,	carbon dioxide	,,	1·98 ,,
∴ 100 c.cm.	of	,,	,,	0·198 ,,

Should the weight of the gas be given, and its volume is to be determined, the second form of expression is more easily applied.

Example 2.—*Required the volume occupied by* 0·5 *grm. of ammonia at* 0° *C. and* 760 *mm. pressure.*

17 grm.	of ammonia	occupy	22·22 litres.
1 ,,	,,	occupies	1·307 ,,
0·5 ,,	,,	,,	0·653 ,,

It is useful also to bear in mind that air is 14·435 times as heavy as hydrogen, since frequently the densities of vapours as actually determined by experiment are stated in terms of air as unit.

Thus the density of sulphur dioxide is found by experiment to be 2·247, air being the unit. The density compared with hydrogen is therefore $2{\cdot}247 \times 14{\cdot}435$, or 32·43, a value agreeing well with that deduced from the accepted composition of this gas.

69. Correction for Temperature and Pressure.—We shall first consider the influence of variations of *temperature* on the volume of a gas, and consequently on the weight of a given volume.

We have seen (Chap. V.) that a gas at 0° C. expands $\frac{1}{273}$ of its volume for each increment of one degree Centigrade in temperature. The more general form of expression, viz. that the volume of the gas is proportional to the absolute temperature (see § 30), will be found the most useful, as a few examples will show. In order to make the calculation it is, in the first place, necessary to convert the temperatures as ordinarily stated into absolute temperatures.

Example 3.—*A litre of gas is measured at 0° C.; what volume will it occupy at — 20° C., and what at 50° C.?*

$$0° \text{ C.} = 273° \text{ absolute.}$$
$$-\ 20° \text{ C.} = 253° \quad ,,$$
$$+\ 50° \text{ C.} = 323° \quad ,,$$

Volume required is at — 20° C. $1 \text{ litre} \times \frac{253}{273} = 926{\cdot}8 \text{ c.cm.}$

,, ,, ,, + 50° C. $1 \text{ litre} \times \frac{323}{273} = 1183{\cdot}2 \text{ c.cm.}$

Example 4.—*The volume of a gas measured at 10° C. is found to be 150 c.cm.; what volume would it occupy at the standard temperature (0° C.)?*

$$10° \text{ C.} = 283° \text{ absolute.}$$

Volume required is at 0° C. $150 \times \frac{273}{283} = 144{\cdot}7 \text{ c.cm.}$

Example 5.—*The volume of a gas measured at* 15° *C. is found to be* 250 *c.cm.; what volume would it occupy at* − 15° *C. and at* 57° *C. respectively?*

$$15° \text{ C.} = 288° \text{ absolute.}$$
$$-15° \text{ C.} = 258° \quad ,,$$
$$+57° \text{ C.} = 330° \quad ,,$$

$$\text{Volume required at } -15° \text{ C.} = 250 \times \frac{258}{288} = 224{\cdot}0 \text{ c.cm.}$$

$$,, \quad ,, \quad ,, \quad +57° \text{ C.} = 250 \times \frac{330}{288} = 286{\cdot}5 \text{ c.cm.}$$

And now let us consider the effect of variation in *pressure*. According to Boyle's Law (see § 28), the volume of a gas is inversely proportional to the pressure to which it is subjected when the temperature is constant.

Example 6.—*A gas measured at standard atmospheric pressure* (760 *mm.*) *is found to occupy* 1·5 *litres; what volume will it occupy at* 1,000 *mm. and at* 100 *mm. pressure?*

$$\text{Required volume at 1000 mm. is } 1500 \times \frac{760}{1000} = 1140 \text{ c.cm.}$$

$$,, \quad ,, \quad ,, \quad 100 \text{ mm. is } 1500 \times \frac{760}{100} = 11400 \text{ c.cm.}$$

Example 7.—*The volume of a gas at* 500 *mm. pressure is found to be* 250 *c.cm.; what would it measure under* 5 *atmospheres pressure?*

$$5 \text{ atmospheres} = (760 \times 5) \text{ mm.} = 3800 \text{ mm.}$$

$$\text{Required volume at 5 atmos.} = 250 \times \frac{500}{3800} = 32{\cdot}9 \text{ c.cm.}$$

Finally, an example is given of the allowance for both temperature and pressure in the same expression, *i.e.* on the application of the gas equation $PV/T = K$.

Example 8.—*A gas occupies* 190 *c.cm. at* 13° *C. and* 740 *mm. pressure; what volume would it occupy at standard temperature and pressure* (0° *C. and* 760 *mm.*), *and what at* − 130° *C. and* 780 *mm. pressure?*

$$13° \text{ C.} = 286° \text{ absolute.}$$
$$0° \text{ C.} = 273° \quad ,,$$

$$\text{Volume at } 0^\circ \text{ C. and } 760 \text{ mm.} = 190 \times \frac{273 \times 740}{286 \times 760} = 176{\cdot}6 \text{ c.cm.}$$

$$-130^\circ \text{ C.} = 143 \text{ absolute.}$$

$$\text{Volume at } -130^\circ \text{ C. and } 780 \text{ mm.} = 190 \times \frac{143 \times 740}{286 \times 780} \text{ c.cm.}$$

$$= 90{\cdot}1 \text{ c.cm.}$$

70. The Relation between Weight and Volume of Liquids.—The specific gravity of liquids is expressed in terms of pure water at 15° C. as unit. The following table shows that the specific gravity of water varies at different temperatures, water at 4° being taken as 1 :—

Specific gravity of water at			0° = 0·99987
,,	,,	,,	2° = 0·99997
,,	,,	,,	4° = 1·00000
,,	,,	,,	10° = 0·99975
,,	,,	,,	15° = 0·99916
,,	,,	,,	20° = 0·99826
,,	,,	,,	25° = 0·99712

In ascertaining the density of a liquid by comparison with water it is more convenient to make the determination at ordinary temperatures, and hence it is usual to adopt the specific gravity of water at 15° C. as the basis of comparison.

When we say that the specific gravity of a liquid is 1·8 we mean that it is heavier than water in the proportion 1·8 : 1 ; if therefore 1 c.cm. of water weighs 1 grm., 1 c.cm. of such a liquid will weigh 1·8 grm.* The following examples will show how specific gravity of liquids enters into chemical problems.

Example 9.—*What is the weight of* 100 *c.cm. of sulphuric acid of specific gravity* 1·84 ?

100 c.cm. of water			weigh	100 grm.
,,	,,	sulphuric acid of the specific gravity given	,,	184 ,,

* This is not strictly accurate, since the gramme is the weight of 1 c.cm. of water *at* 4° *C.* The correction, however, is only made in case a very exact expression is desired, and for ordinary purposes it is omitted. In any case the actual weight may be obtained by multiplying the result by 0·99916.

Example 10.—*Hydrochloric acid of specific gravity* 1·112 *contains* 21 *per cent. by weight of gaseous hydrochloric acid ; find the volume of hydrochloric acid gas at* N.T.P. *in* 10 *c.cm. of such acid.*

By the method used in the previous problem 10 c.cm. of hydrochloric acid will weigh 11·12 grm.

$\therefore \frac{11{\cdot}12 \times 21}{100} = 2{\cdot}3352$ grm. = the weight of gaseous hydrochloric acid contained in it.

36·5 grm. of HCl occupy 22·22 litres at N.T.P. ;

$\therefore$ 2·3352 grm. occupy $\frac{22{\cdot}22 \times 2{\cdot}3352}{36{\cdot}5}$ litres

= 1·421 litres.

71. The Relation between Weight and Volume of Solids.—Like that of liquids this is expressed in terms of water as unit. Thus, diamond is 3·5 times as heavy as water, and its specific gravity is 3·5; the specific gravity of graphite is 2·2, of mercury 13·6.

The weights of these bodies that occupy the same volume as 1 grm. of water (that is, 1 c.cm.) are 3·5, 2·2, and 13·6 grm. respectively.

This relation is seldom necessary in chemical calculations.

72. Calculation of the Percentage Composition of a Body.—When the chemical composition of a body is expressed by symbols, the proportions of the respective elements contained in it are the weights of the elements as determined from the table of atomic weights. Thus :—

HCl indicates a compound formed by the union of 1 part by weight of hydrogen with 35·5 parts by weight of chlorine.

H_2O indicates a compound formed by the union of 2 parts by weight of hydrogen with 16 parts by weight of oxygen.

CO_2 indicates a compound formed by the union of 12 parts by weight of carbon with 32 (*i.e.* 2×16) parts by weight of oxygen.

P_2O_5 indicates a compound formed by the union of 62 (*i.e.* 2×31) parts by weight of phosphorus with 80 (*i.e.* 5×16) parts by weight of oxygen.

H_3PO_4 indicates a compound formed by the union of 3 parts by weight of hydrogen, 31 parts by weight of phosphorus, and 64 (*i.e.* 4×16) parts by weight of oxygen.

36·5	parts by weight of	HCl	contain	1 pt. of H and 35·5 pts. of Cl.
18	,, ,,	H_2O	,,	2 pts. ,, H and 16 ,, ,, O.
44	,, ,,	CO_2	,,	12 ,, ,, C and 32 ,, ,, O.
142	,, ,,	P_2O_5	,,	62 ,, ,, P and 80 ,, ,, O.
98	,, ,,	H_3PO_4	,,	3 ,, ,, H, 31 of P and 64 of O.

The *percentage* composition is merely the statement of the relative weights of each of the constituents in 100 *parts* of the compound. Thus, if 18 parts by weight of water contain 2 parts of hydrogen and 16 parts of oxygen, then 100 parts of water will contain—

$$\frac{2 \times 100}{18} \text{ parts of H, } \textit{i.e.}\ 11{\cdot}11\ ;$$

$$\text{and } \frac{16 \times 100}{18} \text{ ,, ,, O, } \textit{i.e.}\ 88{\cdot}88\ ;$$

and this represents the percentage composition of water.

Example 11.—*Find the percentage composition of potassium chlorate,* $KClO_3$—

$$\begin{aligned} K &= 39{\cdot}0 \\ Cl &= 35{\cdot}5 \\ O_3 &= 48{\cdot}0 \\ \hline & 122{\cdot}5 \end{aligned}$$

$$\therefore \text{ Percentage amount of K} = \frac{39{\cdot}0 \times 100}{122{\cdot}5} = 31{\cdot}84$$

$$\text{,, ,, Cl} = \frac{35{\cdot}5 \times 100}{122{\cdot}5} = 28{\cdot}98$$

$$\text{,, ,, O} = \frac{48 \times 100}{122{\cdot}6} = 39{\cdot}18$$

$$100{\cdot}00$$

Example 12.—*Find the percentage amount of water of crystallisation in* $FeSO_4 + 7\ H_2O$.

$$\begin{aligned} Fe &= 56 \\ S &= 32 \\ O_4 &= 64 \\ 7\ H_2O &= 126 \\ \hline & 278 \end{aligned}$$

278 parts of $FeSO_4 + 7\ H_2O$ contain 126 parts of water.

$$\therefore \text{ Percentage of water} = \frac{126 \times 100}{278} = 45{\cdot}32.$$

73. Determination of the Formula of a Substance.—The question which even more frequently arises in practice is the converse one, the determination of the formula of a substance from the results of analysis of the substance. We have seen already that the relative composition by weight of a body is obtained by taking the atomic weight of each constituent, and where more than one atom of any constituent is present, then the multiple of that according to the number of atoms. Thus for $COCl_2$—

	Atomic Weight.	No. of Atoms.	Product.	Percentage Composition.
C	12	1	12	12·12
O	16	1	16	16·16
Cl_2	35·5	2	71	71·72

We now reverse the process, and desire to determine the relative number of atoms of each element, having given the composition by weight of a body as deduced from its analysis—

S = 23·7 per cent.
O = 23·7 „ „
Cl = 52·6 „ „

Let n, n', n'' be the number of atoms of S, O, and Cl respectively, the atomic weights being 32, 16, and 35·5; we have the relative weights of each of the constituents—

$32\,n$, $16\,n'$, and $35{\cdot}5\,n''$.

These values are proportional to the weights as represented by the percentage composition, viz.—

$$23{\cdot}7,\ 23{\cdot}7,\ 52{\cdot}6.$$

Thus—

$32\,n \propto 23{\cdot}7$ and n is proportional to $\frac{23{\cdot}7}{32}$ or 0·74.

$16\,n' \propto 23{\cdot}7$ „ n' „ „ $\frac{23{\cdot}7}{16}$ or 1·48.

$35{\cdot}5\,n'' \propto 52{\cdot}6$ „ n'' „ „ $\frac{52{\cdot}6}{35{\cdot}5}$ or 1·48.

The *simplest proportion in whole numbers* is—

$$1 : 2 : 2,$$

and the formula on this assumption is—

$$SO_2Cl_2.$$

This, then, is the *empirical formula* as deduced solely from the consideration of the results of the analysis. It is quite consistent with such a calculation that the formula should be $S_2O_4Cl_4$, or $S_3O_6Cl_6$, or any such multiple. Which of these is to be finally accepted can only be decided after a determination of the vapour density of the body, or of its chemical constitution and character, and this would be the *molecular formula* of the body.

To determine the empirical formula of a body, we therefore divide the results of analysis by the respective atomic weights, and the numbers so obtained are *proportional* to the number of atoms.

Example 13.—*The percentage composition of a compound is found to be* H = 5·88 *and* O = 94·12 : *find its formula.*

In this case n and n' being in proportion to the number of atoms of hydrogen and oxygen respectively—

nH = 5·88, and H being 1, n = 5·88 ;

n'O = 94·12, and O being 16, n' = 5·88.

∴ Simplest formula = HO.

The body in Example 13 consists of an equal number of atoms of H and O, and the simplest formula is HO. Chemical considerations, however, compel us to accept a multiple of this, viz. H_2O_2, as the formula of hydrogen peroxide, the substance which has this composition.

Example 14.—*Find the formula of a substance having the composition*—Mg = 9·76, S = 13·01, O = 26·01, *and water of crystallisation* = 51·22.

Mg gives $\frac{9{\cdot}76}{24} = 0{\cdot}406$ as proportional number.

S „ $\frac{13{\cdot}01}{32} = 0{\cdot}406$ „ „

O „ $\frac{26{\cdot}01}{16} = 1{\cdot}626$ „ „

H_2O „ $\frac{51{\cdot}22}{18} = 2{\cdot}846$ „ „

From these numbers we deduce as the simplest whole numbers bearing the same relation to one another 1 : 1 : 4 : 7, and the simplest formula for the body is—

$$MgSO_4 + 7\,H_2O.$$

74. Application to Chemical Problems.—We have now considered the fundamental calculations which enter into chemical problems, and a few examples will be given to show how these bear upon questions involving chemical decomposition and interchange.

Example 15.—*What weight of caustic soda* (NaOH) *will be needed to just neutralise* 10 *c.cm. of dilute sulphuric acid* (*specific gravity* 1·155) *containing* 21 *per cent. of* H_2SO_4?

In all cases where a chemical reaction is concerned, involving considerations of weight or volume, it is well to state the reaction in the form of an equation at the outset—

$$2\,NaOH + H_2SO_4 = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + 2\,H_2O.$$

From this we see that 2 NaOH neutralise H_2SO_4, the respective weight relations being—

$$2\,(23 + 16 + 1) \text{ and } (2 + 32 + 64) \text{ or } 80 : 98.$$

i.e. 80 parts by weight of caustic soda serve to neutralise 98 parts by weight of sulphuric acid.

Now determine the actual weight of sulphuric acid that is to be neutralised—

10 c.cm. of the dilute sulphuric acid (specific gravity 1·155) weigh 11·55 grm.

21 per cent. of this is H_2SO_4, *i.e.* $\frac{11{\cdot}55 \times 21}{100} = 2{\cdot}4255$ grm.

∴ Required amount of caustic soda is—

$$\frac{2{\cdot}4255 \times 80}{98} \text{ grm., or } 1{\cdot}98 \text{ grm.}$$

Example 16.—*What volume of oxygen collected at standard temperature and pressure* (0° *and* 760 *mm.*) *is given off on heating* 10 *grm. of mercuric oxide?*

The equation representing the action of heat on mercuric oxide is—

$$2\,HgO = 2\,Hg + O_2.$$

First determine the *weight* of oxygen from the above equation, which shows that 432 parts of mercuric oxide yield 32 parts of oxygen, or, in simpler numbers, 27 parts yield 2 parts of oxygen.

$$10 \text{ grm. therefore yield } \frac{2 \times 10}{27}, \text{ or } 0{\cdot}74 \text{ grm.}$$

Now 32 grm. of oxygen occupy at standard temperature and pressure 22·22 litres, and the *volume* of oxygen corresponding to this weight is—

$$\frac{0{\cdot}74 \times 22{\cdot}22}{32} = 0{\cdot}514 \text{ litres} = 514 \text{ cub. cm.}$$

Example 17.—*What weight of sulphur must be burnt so as to yield* 1 *litre of sulphur dioxide at standard temperature and pressure?*

$$S + O_2 = SO_2.$$

Here we start from a known *volume* of gas and must work back to the *weight* in terms of which the result is to be expressed.

22·22 litres of SO_2 weigh 64 grm. (N.T.P.).

$$1 \text{ litre of } SO_2 \text{ weighs } \frac{64}{22{\cdot}22} \text{ or } 2{\cdot}869 \text{ grm.}$$

Also 64 grm. of SO_2 contain 32 grm. of S,

and 2·869 „ SO_2 „ 1·4345 „ S.

∴ 1·4345 grm. of sulphur will therefore be required to produce 1 litre of SO_2 at N.T.P.

Such a calculation as Example 17 may, however, be shortened by the consideration that as 32 grm. of sulphur, according to the equation, yield 64 grm. or 22·22 litres of SO_2, at N.T.P.

$$\frac{32}{22{\cdot}22} \text{ grm. will yield 1 litre of } SO_2.$$

The next example will be rendered more complex by introducing conditions of temperature and pressure differing from the standard. No further difficulty is really involved, except that the correction for temperature and pressure must be made.

Example 18.—*2½ litres of nitrous oxide have been collected at 39° C. and 741 mm. pressure; what weight of ammonium nitrate has been decomposed in order to supply the gas?*

First eliminate the irregularity introduced by the temperature and pressure, by determining what volume the gas would have occupied had it been collected at standard temperature and pressure. This will be—

$$\frac{2{\cdot}5 \times 273 \times 741}{312 \times 760} \text{ litres, or } 2{\cdot}133 \text{ litres.}$$

Now according to the equation—

$$\underset{\text{Ammonium nitrate.}}{NH_4NO_3} = \underset{\text{Nitrous oxide.}}{N_2O} + 2\,H_2O,$$

80 grm. of ammonium nitrate yield 44 grm. (or 22·22 litres) of nitrous oxide, and hence

$$\frac{80 \times 2{\cdot}133}{22{\cdot}22} \text{ grm., or } 7{\cdot}681 \text{ grm. of ammonium nitrate have been decomposed.}$$

Example 19.—*One gramme of water is* (a) *converted into steam at* 100° *C.,* (b) *decomposed by means of sodium and the hydrogen collected at* 13° *C.; what volume will each occupy, the barometer at the time standing at* 750 *mm.?*

First, let us consider the case of the steam. This being water vapour has, at standard temperature and pressure, a density such that, as previously shown,

18 grm. is the weight of 22·22 litres.

$$\text{Thus 1 grm. occupies } \frac{22{\cdot}22}{18} \text{ or } 1{\cdot}234 \text{ litres.}$$

At 100° C. and 750 mm. pressure this occupies—

$$\frac{1{\cdot}234 \times 373 \times 760}{273 \times 750} = 1{\cdot}71 \text{ litres.}$$

Secondly, as to the hydrogen, the decomposition is represented by the equation—

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2;$$

from which we see that 36 grm. of water yield 2 grm. of hydrogen, and therefore 1 grm. of water yields $\frac{1}{18}$ grm. of hydrogen.

The *volume* of hydrogen at standard temperature and pressure is thus $\frac{11{\cdot}11}{18}$ or 0·62 litre. Corrected so as to represent the volume at 13° C. and 750 mm. pressure this becomes—

$$\frac{0{\cdot}62 \times 286 \times 760}{273 \times 750} = 0{\cdot}658 \text{ litre.}$$

Miscellaneous Worked Examples.

The whole of the more important elements entering into the treatment of chemical problems have now been discussed, and it only remains to add some miscellaneous examples in further illustration of their application to chemical reactions.

Example 20.—10 *grm. of mercury are heated with excess of concentrated sulphuric acid and the sulphur dioxide formed is collected at* 15° *C. and* 765 *mm. pressure; what volume does it occupy?*

Here, as in most cases, it is best to commence by a statement of the reaction which takes place.

$$Hg + 2\,H_2SO_4 = \underset{\text{Mercuric sulphate.}}{HgSO_4} + 2\,H_2O + SO_2.$$

200 grm. of mercury give 64 grm. of SO_2,
or 200 ,, ,, ,, 22·22 litres of SO_2.
∴ 10 ,, ,, ,, 1·111 ,, ,,
at standard temperature and pressure.

Volume at 15° C. and 765 mm. pressure is then

$$\frac{1{\cdot}111 \times 288 \times 760}{273 \times 765} = 1{\cdot}164 \text{ litre.}$$

Example 21.—25 *c.cm. of marsh gas* (CH_4) *are mixed with* 500 *c.cm. of air and exploded in a eudiometer; what volume of gas should there be* (a) *before the removal of the carbon dioxide formed,* (b) *after the absorption of the carbon dioxide by means of caustic potash? The temperature and pressure may be assumed to be the same when each of the readings of volume was taken.*

The chemical reaction which takes place is

$$\underset{\text{2 vols.}}{CH_4} + \underset{\text{4 vols.}}{2\,O_2} = \underset{\text{2 vols.}}{CO_2} + 2\,H_2O,$$

the nitrogen of the air taking no part in the combustion.

It is further manifest on inspection that the 2 volumes of marsh gas and 4 volumes of oxygen, before explosion, give rise to 2 volumes of carbon dioxide, the space occupied by the water being negligible.

Thus 6 volumes are reduced to 2, and the diminution is 4 volumes.

But the marsh gas occupies 25 c.cm., and is represented by 2 volumes.

The diminution in volume is therefore 50 c.cm., and the 525 c.cm. of mixed gases originally present in the eudiometer have been reduced to 475 c.cm.

Similarly the CO_2 occupies the same volume as the marsh gas from which it was obtained, and is thus 25 c.cm., and if this be removed there will remain 450 c.cm. of gas in the eudiometer. The result is that the residual gas—

(*a*) before removal of CO_2 is 475 c.cm.
(*b*) after „ „ „ 450 c.cm.

Example 22.—10 *c.cm. of liquid carbon disulphide* (*specific gravity* 2·63) *are burnt in oxygen ; find the volume of the resulting gases measured at standard temperature and pressure.*

We must first ascertain the weight of the carbon disulphide. Its specific gravity being 2·63, the 10 c.cm. will weigh 26·3 grm.

The chemical change during combustion is represented in the equation—

$$CS_2 + 3\,O_2 = CO_2 + 2\,SO_2.$$

76 grm. of CS_2 yield 44 grm. or 22·22 litres CO_2 at N.T.P.
„ „ „ „ 128 „ „ 44·44 „ SO_2 at N.T.P.
„ „ „ „ 66·66 litres of CO_2 and SO_2 together.

$$\therefore\ 26{\cdot}3 \text{ grm. of } CS_2 \text{ yield } \frac{66{\cdot}66 \times 26{\cdot}3}{76} = 23{\cdot}08 \text{ litres at N.T.P.}$$

Example 23.—*Considering air as a mixture of* 79 *per cent. by volume of nitrogen with* 21 *per cent. by volume of oxygen* (i.e. *neglecting argon*), *find the density of air compared with hydrogen. Also find the density of the vapour of carbon disulphide compared with air.*

79 vol. of nitrogen are as heavy as 79 × 14, or 1106 vol. of H.
21 vol. of oxygen are as heavy as 21 × 16, or 336 „ „

100 vol. of air are as heavy as ... ... 1442 „ „

∴ Density of air is 14·42.*

Density of the vapour of disulphide of carbon is $\frac{12 + 64}{2}$ or 38, compared with hydrogen.

Compared with air it is therefore $\frac{38}{14{\cdot}42} = 2{\cdot}635$.

* Actual density at normal composition is taken as 14·435.

Atomic Weights to be used in the Following Calculations.

Hydrogen,	1.	Chlorine,	35·5.
Carbon,	12.	Potassium,	39.
Nitrogen	14.	Calcium,	40.
Oxygen,	16.	Iron,	56.
Sodium,	23.	Bromine,	80.
Magnesium,	24.	Silver,	107·6.
Phosphorus,	31.	Antimony,	119·6.
Sulphur,	32.	Mercury,	200.

Lead, 206·4.

QUESTIONS.—CHAPTER X.

1. The volume of a permanent gas at 0° C. is 3 litres; at what temperature would it occupy 4 litres, the pressure remaining unaltered?

2. Two samples of gas occupy the same volume, but one is at −20° C., and the other at 20° C.; what is their relative volume when both are at 0° C.?

3. The volume of a gas at 13° C. is 100 c.cm.; find its volume at − 130° C., at − 13° C., and at 130 °C.

4. A gas under standard atmospheric pressure measures 209 c.cm.; what volume will it occupy under a pressure of $\frac{1}{10}$, $\frac{1}{2}$, 2, and $5\frac{1}{2}$ atmospheres respectively?

5. What volume will half a litre of gas measured at 750 mm. pressure occupy when subjected to a pressure of 850 mm. of mercury?

6. A rectangular vessel 10 c.cm. long, 5 c.cm. wide, and 3·5 c.cm. deep, is filled with gas at 100° C. and 770 mm. pressure; what volume will the gas occupy at standard temperature and pressure?

7. A sample of gas is collected in a eudiometer, and it is found that the level of the mercury in the eudiometer is 257 mm. above that in the trough; also the height of the barometer at the time is 745 mm.: under what pressure is the gas?

8. A sample of gas is collected at standard temperature and pressure, and the pressure is then doubled and the temperature gradually raised until the volume of the gas is the same as it was originally; at what temperature does this occur?

9. Under how many atmospheres pressure will steam have the same density as water (1 c.cm. weighs one gramme), if the contraction takes place in accordance with Boyle's Law, and the temperature remains at 600° C.?

10. If the temperature remains at zero, at what pressure will hydrogen have a density equal to 0·62 of that of water, this being the density found by Dewar for hydrogenium ?

11. One cubic centimetere of bromine (density 3·2) is transformed into vapour at 78° C., determine the volume occupied by the vapour.

12. The specific gravity of pure nitric acid being 1·522, find the weight of 100 c.cm. of it, and the volume that you must take to weigh 100 grm.

13. What volume of such acid will be required to just neutralise 100 grm. of caustic potash (KOH), and what weight of potassium nitrate is formed ?

14. Calculate the percentage composition of calcium carbonate ; what percentage of carbon dioxide does it contain ?

15. Chlorine forms with water a solid hydrate, having the composition $Cl_2 \cdot 8\ H_2O$; calculate the percentage of hydrogen, chlorine, and oxygen contained in this body.

16. Find the empirical formula of a compound consisting of 46·66 per cent. of iron and 53·33 per cent. of sulphur.

17. An oxide of iron contains 72·3 per cent. of iron ; determine its empirical formula.

18. Determine the simplest formula for a salt having the following percentage composition :—

Sodium	29·36
Phosphorus	26·38
Oxygen	44·26
	100·00

19. A solution of caustic soda having the specific gravity 1·32 contains 28·8 per cent. of NaOH ; what weight of sulphuric acid is required to be just sufficient to neutralise a litre of such a solution ?

20. What volume of sulphuretted hydrogen at 13° C. and 798 mm. pressure is required to effect the complete precipitation of one gramme of corrosive sublimate, $HgCl_2$?

21. What weight of pure antimony sulphide, Sb_2S_3, should yield a litre of sulphuretted hydrogen collected at 10° C. and 760 mm. pressure ?

22. Determine the volume of chlorine required to convert 10 grm. of phosphorus into the pentachloride.

23. A gramme of common salt is dissolved in water and excess of silver nitrate solution is added ; what weight of silver chloride should be precipitated ?

24. Calculate (*a*) the volume, (*b*) the weight, of carbon dioxide in the air of a room 6 m. long, 4 m. wide, and 3 m. high, if there is 1 vol. of this gas present per 1,000 vol. of the air.

25. Dumas determined the relative amounts of nitrogen and oxygen in air by passing it over heated copper. He found—

Weight of tube and copper before experiment	... 120 grm.
,, ,, ,, ,, ,, after ,,	... 121·15 ,,
,, ,, globe when exhausted	... 852 ,,
,, ,, ,, and nitrogen	... 855·85 ,,

From these numbers calculate the percentage composition of air by weight, and deduce its percentage composition by volume.

26. Dumas determined the composition of water synthetically by passing hydrogen over heated copper oxide, and found—

Weight of tube and copper oxide before experiment	... 334·598 grm.
,, ,, ,, ,, ,, ,, after ,,	... 314·236 ,,
,, ,, drying tubes before experiment ...	... 426·358 ,,
,, ,, ,, ,, after ,, ...	... 449·263 ,,

Calculate the percentage composition of water by weight.

27. Ten grammes of steam are passed over red-hot iron ; what volume of hydrogen at 26° C. and 741 mm. pressure will be obtained if one-third of the steam undergoes decomposition ?

28. Fifteen cubic centimetres of ammonia are completely decomposed by electric sparks, and then 40 c.cm. of oxygen are added and the mixed gases exploded ; state the gases present and the volume of each (*a*) just before exploding, (*b*) after exploding.

29. A mixture of ten litres of oxygen with one litre of carbon dioxide is shaken up with 100 c.cm. of water ; determine the volume of each gas that will be dissolved—the barometer at the time standing at 760 mm. and the thermometer at zero.

30. Make the same determination with a mixture of one litre of oxygen and 10 litres of carbon dioxide.

31. A litre of sea-water (specific gravity 1·03) is evaporated to dryness, and found to leave as residue 36·4 grm. of salts ; find the percentage of solid matter in the sea-water.

32. Given that a metre is equivalent to 39·37 in., calculate the number of cubic inches in a litre and the number of litres in a cubic foot.

33. Determine the percentage of carbon in cane-sugar ($C_{12}H_{22}O_{11}$) and the volume of carbon dioxide that results from the combustion of 0·2 grm. of sugar.

34. A mixture of 20 c.cm. of ethylene and 200 c.cm. of oxygen is exploded in a eudiometer; what volume of gas remains after the explosion, and what volume when the carbon dioxide is subsequently removed by absorption with potash?

35. What quantity of crystallised oxalic acid ($C_2H_2O_4 + 2H_2O$), heated with excess of sulphuric acid, will yield 5 litres of gas at standard temperature and pressure?

36. If 50 c.cm. of sulphuretted hydrogen be mixed with excess of chlorine, what volume of hydrochloric acid will be formed, and what weight of sulphur liberated?

37. A gramme of a substance containing carbon is heated with lead oxide, and found to form 10 grm. of metallic lead; what percentage of carbon was present?

38. What weight of iron must be dissolved in dilute sulphuric acid in order to yield sufficient hydrogen to fill a balloon having a capacity of 100 cub. m.?

39. Ten grammes of carbon are burnt in 1,000 litres of air (taking as consisting of 79 vol. of N and 21 of O) at 15° C. and 700 mm. pressure; find the percentage by volume of nitrogen, oxygen, and carbon dioxide in the air after the combustion is complete.

SECTION II.—SYSTEMATIC TREATMENT OF THE NON-METALS.

CHAPTER XI.

HYDROGEN H_2.

75. History.—Hydrogen must have been unconsciously prepared many times by the earlier chemists in their work on metals and acids; but these chemists never collected or studied gases. The recognition of hydrogen as a definite substance, and the systematic study of its properties and the different ways of preparing it, were due almost wholly to Henry Cavendish, who prepared it by the action of dilute sulphuric acid on zinc or iron in 1766.

Cavendish called it "inflammable air," and not only observed the properties of hydrogen itself, but showed that water is the product of its combustion in oxygen—a discovery of the greatest importance, as water had previously been considered an element. Lavoisier called "inflammable air" hydrogen (= water producer) on account of this discovery. Cavendish also measured with surprising accuracy the relative volumes of hydrogen and oxygen that combined together to form water; and showed that the weight of water formed was the sum of the weights of hydrogen and oxygen used.

Probably Cavendish never really understood the compound nature of water, and the far-reaching importance of his own work, because he always thought in terms of the phlogistic theory. It seems that James Watt, the great engineer, was the first to state definitely (1783) that water was a compound of "dephlogisticated air" (oxygen) and "inflammable air" (hydrogen). This opinion, expressed in a letter to Black *before* the publication of Cavendish's results, was based on Watt's knowledge of some of Priestley's experiments.

76. Occurrence.—Hydrogen occurs in the free state as an incandescent gas in the sun. Free hydrogen is found to some extent on the earth; in natural gases and about one part in a million in the atmosphere.

With the exception of oxygen and silicon hydrogen is the most widely distributed element in nature. Water is a compound of hydrogen and oxygen, H_2O; many oils consist of hydrogen and carbon, and these elements, together with oxygen, form the chief constituents of animal and vegetable tissue, and of organic compounds in general.

77. Methods of Preparation.—The various methods may be summarised as follows:—

(1) *Direct Decomposition of Water by Heat.*—On heating water to a high temperature, it undergoes partial decomposition. Grove effected this by passing steam through a porcelain tube heated to 1,000° C.

(2) *Decomposition of Water by the Electric Current.*—On electrolysis, water, to which a little dilute sulphuric acid has been added, is decomposed into hydrogen and oxygen.

(3) *Decomposition of Water by Metals at Ordinary Temperature.*—The metals which will decompose water without the application of heat are comparatively few in number; they comprise the alkali metals (sodium, potassium, lithium, etc.), the metals of the alkaline earths (calcium, strontium, barium), and magnesium (slowly). Only half the hydrogen is liberated, the equation representing the reaction in the case of sodium being—

$$\underset{\text{Sodium.}}{2\,Na} + \underset{\text{Water.}}{2\,H_2O} = \underset{\text{Caustic soda.}}{2\,NaOH} + \underset{\text{Hydrogen.}}{H_2}.$$

Caustic soda (NaOH) is formed and dissolves in the water, rendering it alkaline, as may be shown by pouring red litmus into the liquid.

Exp. 22. Fill a small gas-jar with water and invert it in a trough. Cut off a piece of sodium about the size of a pea, wrap it up in tinfoil of thin sheet lead perforated with a few pinholes, and place it under the gas-jar. Bubbles of hydrogen are now seen to rise apparently from the metal. When bubbles cease to rise place a greased cover over the

mouth of the jar and turn up the latter. Bring a lighted match near and slide the cover to one side. The gas burns with a yellow flame, which is due to the sodium.

Some metals which by themselves cannot decompose water at ordinary temperatures, are able to do so when in contact with certain other metals, as, for example, the zinc-copper-couple. The *zinc-copper-couple* is prepared by immersing granulated zinc in a dilute solution of copper sulphate for a short time, and then removing the product and washing it well with water to remove adhering salts. The zinc-copper-couple slowly liberates hydrogen from the water in which it is immersed without the application of heat. On warming, hydrogen is rapidly evolved; this provides a convenient method of preparing the pure gas. The zinc alone takes part in the reaction; it is converted into zinc oxide, ZnO—

$$Zn + H_2O = ZnO + H_2.$$

Again, zinc will decompose water at ordinary temperatures if it is in contact with platinum. A discussion of the explanation of these contact decompositions is beyond the scope of this work.

(4) *Decomposition of Water by Metals on the Application of Heat.*—Most metals will decompose water provided the temperature is sufficiently high. Iron and zinc, for example, act readily on steam at red heat; copper, however, is an example of a metal which does not act on water under any conditions.

When the metals just referred to decompose water they displace the whole of the hydrogen, and are converted into oxides—

$$3\,Fe + 4H_2O = \underset{\text{Magnetic oxide of iron.}}{Fe_3O_4} + 4\,H_2.$$

$$Zn + H_2O = \underset{\text{Zinc oxide.}}{ZnO} + H_2.$$

Exp. 23. Fit up and arrange the apparatus shown in Fig. 12. It consists of an iron tube a foot or more in length and a little over half-an-inch in diameter, partly filled with iron turnings or small nails. It is fitted properly at the ends with corks, one being pierced by a glass tube bent at right angles and passing into the flask containing a little

water, while through the other projects the delivery tube, cut off as shown above the surface of the water. A piece of rubber tube is slipped over it sufficiently long to deliver the gas into the jar. The iron tube is supported by a clamp and heated by a flat-flame Bunsen burner.

Boil the water briskly in the flask, which should rest on a sand bath. Air will be expelled from the apparatus and will rise in bubbles through the water. When no more bubbles rise, you may then heat the iron tube as strongly as possible and collect the gas.

However, before collecting any gas in the jar you should take care that all the air has been driven out of the apparatus. To test this, collect some of the gas in a test-tube, and bring it mouth downwards to a flame. An explosion shows that air is still mixed with the hydrogen. Wait a short time and test again. When the gas ignites with only a very slight "pop,' you may proceed to fill the jars. *Neglect of this precaution and want of care in keeping flames away from the delivery tube have often caused serious accidents,* because air and hydrogen form an explosive mixture.

Steam passes over the red-hot nails, and hydrogen can be collected in the jar. When sufficient gas has been collected, first remove the rubber portion of the delivery tube, then the Bunsen with spreading flame, and lastly, when the iron tube is no longer red-hot, the Bunsen underneath the flask.

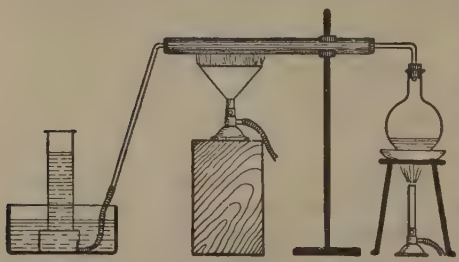


Fig. 12

Note.—The water in the flask must be kept boiling while the gas is being collected, or water may be forced back into the iron tube and cause a slight explosion. If it should cease to boil, at once remove the rubber portion of the delivery tube.

Turn out the residue in the tube and examine it. The turnings or nails are coated with oxide of iron (the so-called "smithy scales" which form on the blacksmith's anvil also consist of it).

(5) *Action of Acids on Metals.*—Many metals act on dilute hydrochloric acid or dilute sulphuric acid with evolution of hydrogen. The common laboratory method of preparing the gas is to act on granulated zinc with dilute sulphuric acid.

Exp. 24. Introduce into a 12-oz. flask, fitted with safety funnel and delivery tube as shown in Fig. 13, 10 grm. of zinc, and add 180 c.cm. of

dilute sulphuric acid. Bubbles of hydrogen will be observed to rise at the zinc, and the gas passing out of the delivery tube may be collected in glass cylinders as shown, *taking the precautions referred to in Exp.* 23.

The equation representing the reaction in the case of zinc is—

$$\underset{}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + H_2.$$

(6) *Action of Alkalies on Metals.*—A few metals, notably zinc and aluminium, are acted upon by a boiling solution of caustic potash or caustic soda with liberation of hydrogen. If zinc and caustic potash are used, the reaction which takes place is represented by the equation—

$$Zn + 2\,KOH = \underset{\text{Potassium zincate.}}{Zn(OK)_2} + H_2.$$

78. Purification of Hydrogen.—The gas obtained by the common laboratory method (Method (5)) is by no means pure; it may contain any or all of the following impurities: *nitrogen* and *oxygen* (derived from the air dissolved in the sulphuric acid), *sulphur dioxide*, SO_2; *sulphuretted hydrogen*, H_2S; *carbon dioxide*, CO_2; *arseniuretted hydrogen*, AsH_3 (if the zinc or acid contains arsenic); *phosphoretted hydrogen*, PH_3 (if the zinc or acid contains phosphorus); *oxides of nitrogen* (if the acid contains nitric acid or oxides of nitrogen) and *water vapour*.

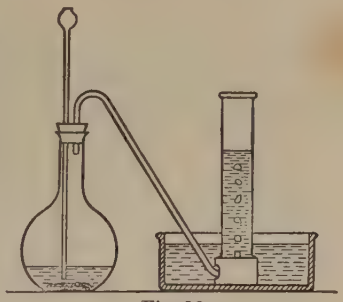


Fig. 13.

In their classical experiments on the composition of water (see § 111), Dumas and Stas obtained pure hydrogen by passing the gas evolved from zinc and dilute sulphuric acid through a series of U-tubes containing the following absorbents in the order given: (1) pieces of glass moistened with a solution of lead nitrate, $Pb(NO_3)_2$; (2) pieces of glass moistened with a solution of silver sulphate, Ag_2SO_4; (3) pieces of pumice stone

moistened with a solution of caustic potash, KOH; (4) solid caustic potash; (5) phosphorus pentoxide, P_2O_5.

Lead nitrate removes sulphuretted hydrogen—

$$H_2S + Pb(NO_3)_2 = \underset{\text{Lead sulphide.}}{PbS} + 2\,HNO_3.$$

Silver sulphate removes arseniuretted hydrogen and phosphoretted hydrogen; these are oxidised into arsenious acid and phosphoric acid respectively—

$$AsH_3 + 3\,Ag_2SO_4 + 3\,H_2O = 6\,Ag + 3\,H_2SO_4 + \underset{\text{Arsenious acid.}}{H_3AsO_3}.$$

$$PH_3 + 4\,Ag_2SO_4 + 4\,H_2O = 8\,Ag + 4\,H_2SO_4 + \underset{\text{Phosphoric acid.}}{H_3PO_4}.$$

Caustic potash absorbs sulphur dioxide, carbon dioxide, and nitrogen peroxide—

$$SO_2 + 2\,KOH = \underset{\text{Potassium sulphite.}}{K_2SO_3} + H_2O.$$

$$CO_2 + 2\,KOH = \underset{\text{Potassium carbonate.}}{K_2CO_3} + H_2O.$$

$$2\,NO_2 + 2\,KOH = \underset{\text{Potassium nitrite.}}{KNO_2} + \underset{\text{Potassium nitrate.}}{KNO_3} + H_2O.$$

It also removes the greater part of the water vapour, being a very hygroscopic substance.

Phosphorus pentoxide absorbs the last traces of moisture—

$$P_2O_5 + H_2O = \underset{\text{Metaphosphoric acid}}{2\,HPO_3}.$$

To prevent as far as possible the presence of nitrogen and oxygen, which are difficult to remove, the sulphuric acid used is previously boiled to expel air.

The best laboratory method for the preparation of *pure* hydrogen, consists in acting on magnesium with dilute sulphuric acid. The gas should be dried by passing through a small flask containing strong sulphuric acid, and may be collected over mercury at the pneumatic trough.

79. Industrial Preparation of Hydrogen.—Most of the hydrogen of commerce is obtained as a by-product in electrolytic processes. Thus in the electrolysis of sodium chloride,

chlorine, caustic soda, and hydrogen are obtained. It has been found that by the electrolysis of alkalies rather than acids a purer product is obtained.

The *silicol* process depends on the decomposition of ferro-silicon by a solution of caustic soda.

$$FeSi + 2\,NaOH + H_2O = Fe + Na_2SiO_3 + 2\,H_2.$$

This method has been used by the military authorities, because alkali is more portable than acid.

In the *Hydrolith* process calcium hydride (hydrolith) is treated with water—

$$CaH_2 + 2\,H_2O = Ca(OH)_2 + 2\,H_2.$$

This method has also been used for military purposes, and in some chemical industries.

Hydrogen is also obtained from water gas—

$$C + H_2O = CO + H_2$$

by passing it directly into a Linde liquid air machine, where the carbon monoxide and other impurities are liquefied.

Another method which has been used fairly extensively depends on the *decomposition of steam by iron*—

$$3\,Fe + 4\,H_2O \rightleftharpoons Fe_3O_4 + 4\,H_2.$$

This reaction is reversible and proceeds in one direction or the other according as water vapour or hydrogen is in excess. Many modifications have been proposed, and in one, which has been applied successfully, the resulting oxide of iron is alternately reduced to metallic iron by means of "water gas" during a period of twenty minutes, and the steam is then passed again for a period of ten minutes at a temperature of 650° C. The carbon monoxide is absorbed by a mixture of lime and potash—

$$KOH + CO = HCO_2K$$

and the resulting potassium formate gives hydrogen on heating to 300° C.—

$$HCOOK + KOH = K_2CO_3 + H_2.$$

80. Properties : Uses.—Hydrogen is a colourless, odourless gas, only very slightly soluble in water, 1 c.cm. of which dissolves about 0·02 c.cm. of the gas at ordinary temperatures.

It is the lightest substance known, its *absolute density*, *i.e.* the weight of one cubic centimetre of it under standard conditions of temperature and pressure, being only 0·00009 grm. The density of air under the same conditions is about 14·4 times that of hydrogen.

The extreme lightness of hydrogen as compared with air is shown by the fact that hydrogen can be poured *upwards* from one vessel into another, or can be collected by upward displacement. If a beaker is suspended upside down from a balance and counterpoised, and hydrogen is then poured upwards into it so as to displace the air, the beaker will show a decrease of weight. Again, if a gas-jar of hydrogen stands mouth upwards, and a light is applied, the whole of the gas burns in one or two seconds, owing to the rapidity with which the hydrogen rises through the denser air; in an inverted gas-jar, on the other hand, the gas burns far more slowly, as it does not then mix with the air.

Hydrogen burns in air or oxygen with a blue non-luminous flame, which is very hot. A solid infusible substance placed in the flame becomes white hot, and emits a brilliant light. This is the principle of the *limelight*, in which a jet of hydrogen (or coal-gas) burning in oxygen impinges on a cylinder of quicklime and raises it to a white heat.

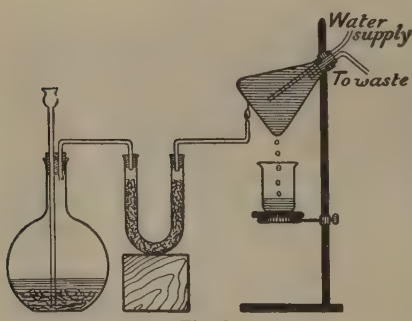


Fig. 14.

In burning, hydrogen combines with oxygen, forming water—

$$2\,H_2 + O_2 = 2\,H_2O.$$

This can be shown readily by means of the apparatus given in Fig. 14. The U-tube contains calcium chloride, and the apparatus should be free from air before lighting the hydrogen at the jet.

A mixture of hydrogen with oxygen or air is violently

explosive, as the combustion is practically instantaneous. Hence care has to be taken in experiments with hydrogen not to apply a light to the gas or to heat any part of the apparatus till all the air has been expelled.

Hydrogen will not support the combustion of those substances which burn in air. Thus a lighted taper is extinguished on being pushed up into an inverted gas-jar of hydrogen; the gas of course takes fire and burns at the mouth of the jar. Burning sulphur and phosphorus are similarly extinguished.

Hydrogen is used for filling airships and balloons, for the production of the oxyhydrogen flame, and in the preparation of quick drying varnishes. It is also used in the reduction of oils into fats, *e.g.* in margarine manufacture. Water gas (§ 431) used as a fuel, and coal gas both contain a large amount of hydrogen.

81. Accurate Determination of the Density of Hydrogen.—The most accurate method of determining the density of hydrogen consists in directly weighing a known volume of the pure gas which is contained in a large globe. The details of the process are as follows :—

Two exactly similar glass globes, of about 10 litres capacity, provided with stopcocks, are taken. One of these is merely used as a counterpoise for the other in weighing, thus avoiding all sources of error due to changes in the temperature or pressure of the atmosphere, for all such changes affect both globes equally. The other globe is exhausted as completely as possible by an air-pump, and then filled with hydrogen which has been carefully dried by passing through U-tubes containing pumice moistened with strong sulphuric acid. The globe is then again exhausted and again filled with dry hydrogen; when this process has been repeated several times all traces of air will have been removed.

Whilst being exhausted and filled for the last time the globe is immersed in melting ice to reduce its temperature to 0° C.; also, in order that the pressure of the hydrogen in the globe may be atmospheric, momentary connection is made with the atmosphere after filling, by opening the stopcock and quickly closing it again. After the adhering water has been wiped off

carefully and the globe has regained the temperature of the atmosphere, it is suspended from one arm of a balance, and the counterpoising globe is hung on the other arm. By placing weights (W_1, say) in the scale pan below the hydrogen globe till equilibrium is restored, the difference in weight between the two globes is found.

The hydrogen globe is now removed from the balance and exhausted as completely as possible; it is then again hung on the arm of the balance and the difference in weight (W_2, say) between the globes again ascertained. Then, neglecting the small amount of hydrogen left in the globe,* the weight of a volume of hydrogen at 0° C. and atmospheric pressure (say, P) equal to the volume of the globe is $W_2 - W_1$. Let the volume of the globe be V c.cm. Then :—

V c.cm. of hydrogen at 0° C. and P mm. pressure weigh

$$W_2 - W_1 \text{ grm.}$$

$\therefore$ V c.cm. of hydrogen at 0° C. and 1 mm. pressure weigh

$$\frac{W_2 - W_1}{P} \text{ grm.}$$

$\therefore$ V c.cm. of hydrogen at 0° C. and 760 mm. pressure weigh

$$\frac{(W_2 - W_1)}{P} 760 \text{ grm.}$$

$\therefore$ 1 c.cm. of hydrogen at 0° C. and 760 mm. pressure weighs

$$\frac{(W_2 - W_1)}{P \times V} 760 \text{ grm.}$$

$\therefore$ density $= \frac{(W_2 - W_1)}{P \cdot V} 760$ grm. per c.cm. at N.T.P.

The same method may be used for finding the density of other gases.

82. The Standard of Atomic Weights.—Owing to its lightness, the weight of an atom of hydrogen was formerly taken as the standard in terms of which the atomic weights of other

* This must be allowed for in very accurate determinations.

elements were expressed. This was unsatisfactory, because until quite recently the *exact* proportion by weight in which oxygen and hydrogen combine was unknown. Also, very few of the elements form stable compounds with hydrogen, whereas the majority do so with oxygen. Therefore, the atomic weight of an element must, in most cases, be first found directly in terms of oxygen and then calculated in terms of hydrogen, using the ratio hydrogen : oxygen determined by analysis of water. It follows that the values for the atomic weights of the majority of the elements depended upon an uncertain ratio. Hence it was decided to take the atomic weight of *oxygen* as standard with a value 16, and this is invariably done at the present time.

The ratio of hydrogen to oxygen in water has been determined with great exactness by E. W. Morley and others, and found to be 1·008 : 8 or 1 : 7·94. When we take oxygen as standard with an atomic weight 16, H = 1·008 (since the molecule of water contains two atoms of hydrogen and one atom of oxygen (H_2O) and $H_2 : O = 2 \times 1{\cdot}008 : 16 = 1{\cdot}008 : 8$). Aston has obtained, by means of the mass spectrograph, the value 1·008 for the atomic weight of hydrogen.

83. Composition of the Hydrogen Molecule.—From a study of the volume composition of gases containing hydrogen, it must be assumed that the molecule of hydrogen contains more than one atom. The question arises, how many atoms does it contain ? We have no means of answering this question *absolutely*, but the following argument renders it exceedingly probable that the number is 2.

No one has so far succeeded in replacing the hydrogen in hydrochloric acid by a metal in two successive stages, as can be done, *e.g.* in the case of sulphuric acid. Now it seems very unlikely that, if hydrochloric acid contains more than one atom of hydrogen in its molecule, *e.g.* if it has such a formula as H_2Cl_2, we should be unable to obtain more than one compound from it, by the action of a metal. Thus, by the action of sodium on H_2Cl_2, we should expect to get one compound, $NaHCl_2$, containing both sodium and hydrogen, and another compound, Na_2Cl_2, containing sodium and no hydrogen.

Hydrochloric acid has, then, most probably, the simple formula HCl.

Now it is found experimentally that *one* volume of hydrogen and *one* volume of chlorine yield *two* volumes of hydrochloric acid, *i.e.* assuming the truth of Avogadro's hypothesis (see § 40), *one* molecule of hydrogen and *one* molecule of chlorine yield *two* molecules of hydrochloric acid. Therefore, one molecule of hydrogen contains as many atoms of hydrogen as two molecules of hydrochloric acid, *i.e.* 2, if the formula for hydrochloric acid is HCl.

84. Occlusion of Hydrogen by Metals.—When certain metals, notably palladium, platinum, and iron, are heated in an atmosphere of hydrogen they absorb the gas to a greater or less extent, and do not lose it on cooling. This phenomenon is termed *occlusion*. The amount of gas taken up depends to some extent on the physical state of the metal—whether it is in the form of a solid mass or of a fine powder. Palladium absorbs far more hydrogen than any other metal; even at the ordinary temperature it takes up 376 times its volume of the gas, and at a red heat more than 900 times its volume. The absorption is accompanied by an increase in volume, but the appearance of the metal is not changed, nor are its properties materially altered; its conductivity for heat and electricity is, however, somewhat decreased whilst it becomes more magnetic.

From a consideration of these facts Graham was led to the conclusion that the hydrogen had become solid and, behaving like a metal, had formed an *alloy* with the palladium. To this solid hydrogen he gave the name *hydrogenium* to indicate its metallic properties—the termination *-um* being used to denote a metal.

Troost and Hautefeuille, as a result of their researches, stated that a *definite compound* of palladium and hydrogen, Pd_2H, palladium hydride was formed; but this is not generally accepted.

The still more recent work of Dewar on solid hydrogen has shown that Graham's conclusions were wrong, for solid hydrogen has been found to possess the properties of a non-metal rather than of a metal.

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The exact nature of palladium hydride must be considered as, at present, unsolved.

Active Hydrogen.—By heating a filament of tungsten, platinum, or palladium to a high temperature in hydrogen at low pressure " active " hydrogen is formed, which is supposed to be monatomic. It is very reactive. Another form of active hydrogen, triatomic hydrogen, H_3, has been prepared by passing an electric discharge through hydrogen at low pressures.

85. Hydrides.—Hydrogen forms compounds with all the non-metals (either directly or indirectly) and with many of the metals; these compounds are called hydrides. The hydrides of the non-metals are, as a whole, stable compounds, but those of the metals are unstable. Examples of non-metallic hydrides are hydrogen chloride, HCl, water, H_2O, ammonia, NH_3, and marsh gas, CH_4. The chief hydrides of the metals are potassium hydride, KH, sodium hydride, NaH, and copper hydride, Cu_2H_2. The most important hydride is water.

86. Conditions under which Hydrogen and Oxygen Combine.—Hydrogen burns in oxygen to form water; it has been found, however, that *perfectly dry* hydrogen will not burn in *perfectly dry* oxygen. In other words, a small amount of moisture must be present in order that combination may take place. We shall meet in the following pages with a number of other examples of this phenomenon, namely, the inability of substances to combine in the entire absence of moisture.

87. Catalysis.—Under ordinary conditions hydrogen and oxygen can only combine directly at high temperatures, but in contact with certain substances, such as platinum sponge, combination is brought about at the ordinary temperature. The platinum does not suffer any change, and belongs to a class of substances called **catalysts.** These are substances which *by contact* are able to hasten a reaction between other substances, but at the end of the reaction are themselves unchanged. The process is known as **catalysis,** and we shall meet with numerous other examples as we proceed.

It is supposed that these reactions do take place *infinitely slowly* in the absence of the catalyser, *i.e.* the catalyser does not start them but makes them proceed very much faster. The phenomenon of catalysis is fully discussed in *Inorganic Chemistry, Mainly Metals.*

88. Reducing Agents.—Hydrogen is able to remove the oxygen from many hot metallic oxides with formation of water. In such reactions hydrogen is said to *reduce* the oxide to the metal, and hydrogen is spoken of as a *reducing agent.* Some examples are as follows :—

(1) $CuO + H_2 = Cu + H_2O$

(2) $As + 3H = AsH_3$ (Marsh's Test, see *Inorganic Chemistry, Mainly Metals*).

(3) $FeCl_3 + H = FeCl_2 + HCl$.

Examples (2) and (3) are brought about by agents liberating hydrogen, *i.e.* nascent hydrogen, and not by hydrogen gas under the ordinary conditions.

The original criterion of a reducing agent was its power of removing oxygen from a compound, but the term has now acquired an extended meaning. For example, in the reaction—

$$HgCl_2 + Hg = Hg_2Cl_2$$

the mercuric chloride is said to be reduced to mercurous chloride by the action of metallic mercury. Similarly, in the case of—

$$2\,FeCl_3 + SnCl_2 = 2\,FeCl_2 + SnCl_4$$

the ferric chloride is said to be reduced to ferrous chloride, and the stannous chloride is then oxidised to stannic chloride.

We can now give the following definition :—*A reducing agent is a substance which is able to bring about a decrease in the ratio of the non-metallic or electro-negative to the metallic or electro-positive part of another substance.*

89. Liquid and Solid Hydrogen.—The enormous difficulties which have attended the attempts of experimenters to reduce hydrogen to the liquid state were overcome by Olszewski,

who was the first to accomplish the task, but it is to Dewar that we owe the production of liquid hydrogen in any quantity.

The method of liquefying hydrogen consists in cooling the gas under great pressure to about — 200° C. by means of boiling liquid air, and then allowing the cooled gas to expand suddenly through a small orifice. During the expansion heat is absorbed,* and this further lowers the temperature to the point of liquefaction of hydrogen. Liquid hydrogen is a colourless substance which boils at — 252° C. It has a specific gravity 0·07, and is thus by far the lightest liquid known.

On allowing liquid hydrogen to boil rapidly under greatly diminished pressure, a still further fall of temperature is produced, and by this means Dewar has succeeded in solidifying hydrogen. Solid hydrogen is a white crystalline solid which melts at — 259° C., a temperature only 14° above the absolute zero.

90. Detection and Estimation of Hydrogen.—Hydrogen can be readily detected by means of its spectrum, which contains four strong lines. It can also be detected by cooling with liquid air in contact with carbon; this liquefies all other gases except the inert gases helium and neon. It can be estimated by oxidation to water.

QUESTIONS.—CHAPTER XI.

1. Write a short history of the element hydrogen.

2. Name some natural substances which contain hydrogen as an essential constituent. Is hydrogen known to occur in the free state?

3. How may water be decomposed without the application of chemical reagents?

4. What metals decompose water—
   (*a*) at ordinary temperature;
   (*b*) at red heat?
Give equations showing the nature of the reaction in each case.

5. How would you prepare pure hydrogen? Describe briefly the method by which Dumas obtained pure hydrogen.

* It is a general property of gases that they absorb heat on expansion.

6. How is hydrogen prepared industrially?

7. If you desire to prepare moderately pure hydrogen in large quantities, what method would you adopt?

8. Devise three experiments suitable for illustrating in a striking manner the extreme lightness of hydrogen.

9. State the chief properties of hydrogen, dividing them into (*a*) physical properties and (*b*) chemical properties.

10. Describe the method by which the density of hydrogen has been accurately determined.

11. Discuss the relative advantages and disadvantages of adopting hydrogen or oxygen as the standard of atomic weights.

12. The molecule of hydrogen is supposed to contain two atoms. What evidence is there in support of this?

13. Name three metallic and three non-metallic hydrides, and give their formulae.

14. Under what conditions do oxygen and hydrogen combine to form water?

15. What do you understand by the term *catalysis*?

16. Explain what is meant by a *reducing agent*.

17. How have liquid and solid hydrogen been prepared, and what are their properties?

18. In an experiment to determine the density of oxygen by Lord Rayleigh's method (see § 81) the following results were obtained—

Difference between weight of globes, one full of air and the other of oxygen (the air globe being the lighter... 0·101 grm.

Difference between weight of globes after exhausting the oxygen globe ... ... 11·181 grm.

Volume of each of the globes ... ... 8 litres.

Pressure of the atmosphere at the time of the experiment ... ... 750 mm.

Calculate from these data the absolute density of oxygen.

[N.B. Neglect the small amount of oxygen remaining in the globe after exhaustion.]

CHAPTER XII.

OXYGEN AND OZONE.

Oxygen O_2.

91. History.—Oxygen was first isolated in 1774 by Priestley in England, and by Scheele in Sweden. Though working quite independently, they both obtained oxygen by heating mercuric oxide : Scheele also obtained it from other oxides and from nitre. It was called oxygen by Lavoisier on account of its property of forming acids.

The discovery of oxygen was of the highest importance as it quickly enabled correct views to be obtained of the composition of air and water ; and, by the aid of Lavoisier, this discovery also overthrew the phlogiston theory of combustion. As this erroneous theory had dominated chemistry since the beginning of the eighteenth century, it will be well to give a short account of it here.

92. Phlogiston.—The phlogiston theory was due chiefly to a German chemist named Stahl (1660-1734), who, however, probably derived some of his ideas from his countryman Becher (1635-1682). Thomson's *History of Chemistry* says—

" It was conceived by Becher and Stahl that all *combustible* bodies are compounds. Combustibility, according to their view of the subject, depends upon a principle or material substance, existing in every combustible body, and dissipated during the combustion. Stahl invented the term *phlogiston* to denote this common principle of combustible bodies. . . . When lead is kept nearly at a red heat in the open air for some time, it is converted into the beautiful pigment called *red lead* ; this is a calx of lead. To restore this calx again to the state of metallic lead, we have only to heat it in contact

with almost any combustible matter whatever. Coal, peat, charcoal, sugar, flour, iron, zinc, etc., all these bodies, then, must contain one common principle, which they communicate to red lead, and by so doing convert it into lead. This common principle is phlogiston."

The phlogiston theory was a very considerable advance on any theory of combustion which had preceded it; but it was precisely the reverse of the truth. Thus the formation of red lead, which was attributed to the escape of phlogiston from the lead, is really due to the combination of oxygen with the lead; and the combustible bodies which convert red lead back into metallic lead do so by depriving the red lead of its oxygen, not by giving it phlogiston.

The student may follow the phraseology of the phlogistic period by remembering that loss of phlogiston was equivalent to oxidation; thus chlorine, which is obtained by the oxidation of hydrochloric acid, was called "dephlogisticated marine acid gas," and oxygen itself was named "dephlogisticated air." Conversely, the addition of phlogiston to a body meant what we now call reduction.

Hooke and Boyle had shown about 1660 that substances will not continue to burn in a closed air-space. The reply to this was that the burning ceases because the phlogiston cannot escape. It was also well known that various metals increase in weight on being heated in air, although phlogiston was supposed to escape. This objection was met by the supposition that phlogiston had a negative weight, being repelled instead of attracted by the earth!

Soon after the isolation of oxygen Lavoisier showed (*a*) that mercury, when heated for a long time in a closed air-space, becomes coated with a red powder, and that one-fifth of the volume of the air disappears; (*b*) that the red powder thus formed, when separately heated, gives off oxygen, which occupies one-fifth of the volume of the air in (*a*).

By this and similar experiments, Lavoisier showed that the formation of metallic calces and combustions generally are not due to the escape of phlogiston, but to the combination of the metal or burning substance with one of the constituents of the air.

In 1777 Laviosier published the following statements, which may be said to mark the end of the phlogistic period :—

(1) Substances burn only in pure air.

(2) This air is consumed in the combustion, and the increase in weight of the substance burnt is equivalent to the decrease in weight of the air.

(3) The combustible body is, as a rule, converted into an acid by its combination with the pure air, but the metals are converted into calces.

93. Occurrence.—Oxygen is the most widely distributed of the elements; it constitutes about one-half of the earth's crust. Air contains about 20 per cent. of oxygen, water nearly 90 per cent., and the great majority of minerals consist largely of this element.

94. Methods of Preparation.—(1) Oxygen can be prepared by strongly heating potassium chlorate. The course of the reaction is somewhat complex. Decomposition commences at about 370° C., the changes represented in the two following equations taking place simultaneously—

$$4\ KClO_3 = 3\ KClO_4 + KCl.$$

$$2\ KClO_3 = 2\ KCl + 3\ O_2.$$

At higher temperature the perchlorate is decomposed thus—

$$KClO_4 = KCl + 2\ O_2.$$

It is found that if the potassium chlorate is intimately mixed with certain substances in a fine state of division, the decomposition takes place at a much lower temperature and with greater regularity. Examples of such substances are manganese dioxide, cupric oxide, and finely-divided platinum, and since they are unaltered at the termination of the process we are here dealing with a second case of catalysis.

In practice, manganese dioxide is the substance commonly used, and the laboratory method for the preparation of oxygen which is *not* required particularly *pure*, consists in

heating an intimate mixture of potassium chlorate, with about one-third of its weight of manganese dioxide.

Exp. 25. Weigh out about 10 grm. of potassium chlorate and 3 grm. of manganese dioxide, and grind them together in a mortar till they are thoroughly mixed. Introduce the mixture into a small round-bottomed flask, and set up the apparatus shown in Fig. 15. On heating the mixture to about 300° C., *i.e.* a temperature considerably below the melting-point of potassium chlorate, oxygen is rapidly evolved and may be collected over water.

Explanation of the Action of the Manganese Dioxide.—An attempt has been made to explain the action of the manganese dioxide in the following way :—Manganese is capable of forming oxides in which the percentage of oxygen is higher than in manganese dioxide. Thus the oxide corresponding to potassium permanganate ($KMnO_4$) is manganese heptoxide, Mn_2O_7. It is supposed that the potassium chlorate keeps oxidising the manganese dioxide into potassium permanganate with liberation of chlorine and oxygen—

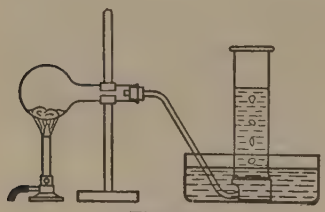


Fig. 15.

$$2\,KClO_3 + 2\,MnO_2 = 2\,KMnO_4 + Cl_2 + O_2.$$

At the temperature of reaction, however, potassium permanganate cannot exist, and immediately reacts with the chlorine thus—

$$2\,KMnO_4 + Cl_2 = 2\,KCl + 2\,MnO_2 + 2\,O_2.$$

The cycle of changes is then repeated.

This explanation is to some extent borne out by facts, for chlorine is always evolved in small quantities, and if only a little manganese dioxide is used the pink colour of potassium permanganate becomes evident.

For ordinary purposes, however, the change which takes place may be expressed by the equation—

$$2\,KClO_3 = 2\,KCl + 3\,O_2.$$

It should be mentioned that no potassium perchlorate is formed when a catalytic agent is used in the decomposition of potassium chlorate.

(2) Many oxides, on heating, evolve oxygen. The equations representing the decomposition of some of them on heating are—

$$2\,HgO = 2\,Hg + O_2.$$
$$2\,Pb_3O_4 = 6\,PbO + O_2.$$
$$2\,Ag_2O = 4\,Ag + O_2.$$
$$4\,CrO_3 = 2\,Cr_2O_3 + 3\,O_2.$$
$$2\,PbO_2 = 2\,PbO + O_2.$$
$$2\,BaO_2 = 2\,BaO + O_2.$$
$$3\,MnO_2 = Mn_3O_4 + O_2.$$

In the case of manganese dioxide the temperature required is much higher than that used in the preparation of oxygen from potassium chlorate and manganese dioxide.

(3) Peroxides, on heating with strong sulphuric acid, yield oxygen—

$$2\,MnO_2 + 2\,H_2SO_4 = 2\,MnSO_4 + 2\,H_2O + O_2.$$
$$2\,PbO_2 + 2\,H_2SO_4 = 2\,PbSO_4 + 2\,H_2O + O_2.$$

(4) Many salts which contain a large percentage of oxygen are decomposed on heating, either alone or in some cases with strong sulphuric acid, with evolution of oxygen. We have already discussed the action of heat on one such salt—potassium chlorate. Another example is potassium nitrate (KNO_3), which on heating loses oxygen and becomes converted into potassium nitrite (KNO_2)—

$$2\,KNO_3 = 2\,KNO_2 + O_2.$$

As illustrations of salts which evolve oxygen on heating with strong sulphuric acid we may take potassium permanganate ($KMnO_4$) and potassium bichromate ($K_2Cr_2O_7$)—

$$4\,KMnO_4 + 8\,H_2SO_4 = 4\,KHSO_4 + 4\,MnSO_4 + 6\,H_2O + 5\,O_2.$$
$$2\,K_2Cr_2O_7 + 10\,H_2SO_4 = 4\,KHSO_4 + 2\,Cr_2(SO_4)_3 + 8\,H_2O + 3\,O_2$$

(5) If bleaching powder is mixed with certain oxides such as cobalt oxide (CoO), or cupric oxide (CuO), and the mixture made into a paste with water, a ready supply of oxygen is obtained on gently heating. Here again the oxide plays the part of a catalytic agent, and the following decomposition takes place :—

$$2\,CaOCl_2 = 2\,CaCl_2 + O_2.$$

(6) Oxygen can be conveniently prepared in the laboratory by the action of water on sodium peroxide (" oxone ")—

$$2\,Na_2O_2 + 2\,H_2O = 4\,NaOH + O_2.$$

95. Manufacture of Oxygen.—Until recently a process known as *Brin's process* was used. This depends upon the fact that when baryta, BaO is heated to *dull redness* in air it takes up oxygen and is converted into the dioxide, BaO_2, which at a *bright red heat* loses the oxygen which it had taken up, and is transformed again into bar ta—

$$2\,BaO + O_2 = 2\,BaO_2.$$

$$2\,BaO_2 = 2\,BaO + O_2.$$

These changes also take place by varying the pressure. This method is no longer worked.

Oxygen is now prepared commercially mainly by liquefying air and then distilling off the more volatile nitrogen. This is described in § 238.

Two processes which may also be mentioned are—

(1) *Electrolytic Process.*—In the manufacture of caustic soda by electrolysis both oxygen and hydrogen are obtained as by products. When aqueous baryta, $Ba(OH)_2$, is used a very pure oxygen is obtained.

(2) *From " Oxygen Cubes."*—Oxygen cubes are tablets made from a mixture of sodium peroxide and bleaching powder. By the action of water oxygen is evolved—

$$CaOCl_2 + Na_2O_2 + H_2O = Ca(OH)_2 + 2\,NaCl + O_2.$$

This method is convenient for small scale work.

96. Properties.—Oxygen is a colourless, odourless gas only slightly soluble in water, 1 c.cm. of which dissolves 0·0489 c.cm. of the gas at 0° C. and 0·034 c.cm. at ordinary temperatures. The weight of 1 c.cm. of oxygen under standard conditions of temperature and pressure, *i.e.* its absolute density, is 0·001429 grm. Since 1 c.cm. of hydrogen weighs 0·00009 grm. under standard conditions, the relative density of oxygen taking hydrogen as unity is $\frac{0{\cdot}001429}{0{\cdot}00009} = 15{\cdot}88$. Taking air as unity the relative density of oxygen is $\frac{0{\cdot}001429}{0{\cdot}0012935}$ = 1·106 (for 1 c.cm. of air under standard conditions weighs ·0012935 grm.), *i.e.* oxygen is slightly heavier than air.

As has already been stated, the atomic weight of oxygen is taken as the standard with the value 16. Since the molecule of oxygen contains two atoms the molecular weight of oxygen is $2 \times 16 = 32$.

The distinguishing feature of oxygen is that it combines readily with nearly all the elements, and often with such energy that the union is accompanied by manifestation of light and heat. This phenomenon is termed "combustion," and oxygen is consequently a *powerful supporter of combustion*. A glowing splinter of wood, if plunged into oxygen, immediately bursts into flame, a property which is only shown by one other gas, nitrous oxide.

The chemical changes which take place when sulphur, phosphorus, carbon, and iron burn in oxygen are represented by the following equations :—

$$S + O_2 = SO_2.$$
Sulphur dioxide.

$$P_4 + 5\,O_2 = 2\,P_2O_5.$$
Phosphorus pentoxide.

$$C + O_2 = CO_2.$$
Carbon dioxide.

$$3\,Fe + 2\,O_2 = Fe_3O_4.$$
Magnetic oxide of iron, or triferric tetroxide.

97. Behaviour of the Metals Towards Oxygen.—This may be concisely indicated in tabular form thus—

Noble Metals.	
Platinum ...	Do not oxidise in air or oxygen. The oxides are unstable and decompose when heated.
Gold	
Silver	
Mercury ...	HgO is formed by gentle heating. At a higher temperature mercuric oxide decomposes.
Base Metals.	
Copper ...	Metal forms CuO on heating.
Lead	Metals burn in oxygen to give PbO, SnO_2, Fe_2O_4
Tin	
Iron	
Zinc	Metal burns in air to form ZnO.
Aluminium .	Metal unaffected.* Amalgam is oxidised in air.
Magnesium .	Metals burn in air to give MgO, Na_2O_2, K_2O_4
Sodium ...	
Potassium ...	

98. Oxidising Agents.—An *oxidising agent* was formerly defined as *a substance which gave up oxygen to other substances.* This definition is now generally extended to include such substances as ferric chloride ($FeCl_3$); thus in the reaction—

$$2\,FeCl_3 + SnCl_2 = SnCl_4 + FeCl_2$$

the stannous chloride is said to be oxidised to stannic chloride and the ferric chloride is reduced to ferrous chloride. This reaction really corresponds to—

$$Fe_2O_3 + SnO = 2\,FeO + SnO_2.$$

We can explain this reaction in terms of valency and ions—

$$2\,Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} = 2\,Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}.$$

Thus the oxidising "ion" loses, and the reducing "ion" gains in valency.

Again, if the electronic view is considered—

$$2\,Fe^{+++} + Sn^{++} = 2\,Fe^{++} + Sn^{++++}$$

* Below 800° C.

the two iron atoms lose two positive charges which are gained by the tin; *but* the loss of a positive charge is really caused by the gain of an electron, which is (or carries) a negative charge. Then we write the equation—

$$2\,Fe^{+++} + 2\,(E) = 2\,Fe^{++}$$

$$Sn^{++} - 2\,(E) = Sn^{++++}.$$

That is, each trivalent Fe atom *gains* an electron (E), and is *reduced*, and each divalent Sn atom *loses* two electrons $2(E)$, and is *oxidised*.

We can then define an **oxidising agent as a substance which is able to bring about an increase in the ratio of the non-metallic or electro-negative to the metallic or electro-positive part of a substance.**

Oxygen is the oxidising agent *par excellence*. Usually, however, oxygen is more active in the presence of finely divided metals, and in the nascent state.

Thus, as an example of the former, we can mention the contact process for the manufacture of sulphuric acid (see § 325)—

$$2\,SO_2 + O_2 = 2\,SO_3.$$

In the case of the latter there are many substances and mixtures which act as oxidising agents when gaseous oxygen has no action. Thus we have—

(i) Nitric acid and sulphuric acid—

$$C + 2\,H_2SO_4 = CO_2 + 2\,SO_2 + 2\,H_2O.$$

These acids give salts with copper, silver, etc., in virtue of their oxidising properties (see §§ 259, 328).

(ii) Potassium dichromate and sulphuric acid, potassium permanganate and sulphuric acid (see § 94).

(iii) Manganese dioxide and lead peroxide—

$$PbO_2 + H_2C_2O_4 + 2\,HNO_3 = Pb(NO_3)_2 + 2\,H_2O + 2\,CO_2$$

Here the oxalic acid is oxidised to carbon dioxide and water.

(iv) Chlorine water and bromine water (see §§ 155, 163).

(v) Ozone and hydrogen peroxide (see §§ 103, 131).

(vi) Electrolytic oxidation. Oxygen is liberated at the anode when water is electrolysed. This fact has been used to bring about oxidation by contact with the anode.

Oxidation frequently occurs by the action of the air at ordinary temperatures. Thus, iron rusts in moist air forming ferric oxide, Fe_2O_3, combined with some water; phosphorus fumes and gives out a faint luminosity in air forming phosphorous oxide, P_4O_6, and other compounds. Organic matter and some mineral substances, such as iron pyrites, also undergo oxidation in the air at ordinary temperatures. This phenomenon of oxidation without the application of heat is often termed *slow combustion*, though the usual manifestations of combustion, viz. the production of light and sensible heat, are, as a rule, absent. As a matter of fact, heat is being given out during these reactions, but so slowly that its production is not apparent.

Oxygen plays an important part in vital processes, both in the animal and vegetable organisms, transforming carbonaceous substances ultimately into carbon dioxide and hydrogenous substances into water. This accounts for the fact that exhaled breath always contains carbon dioxide and water vapour. It is the heat evolved during these processes which maintains the body of an animal at the necessary temperature.

99. The Oxides.—With the exception of fluorine, bromine, and the members of the helium group, all the elements combine with oxygen forming *oxides*. They can be classified as follows :—

(1) Acidic oxides.

(2) Basic oxides.

(3) Peroxides.

(4) Neutral oxides and suboxides.

(1) *Acidic Oxides.*—It was Lavoisier who first showed that the oxides of certain elements (viz. the non-metals), when dissolved in water, form acids. The following equations

represent the reactions which take place when some of these oxides, called *acidic oxides*, combine with water—

$$\underset{\text{Sulphur dioxide.}}{SO_2} + H_2O = \underset{\text{Sulphurous acid.}}{H_2SO_3}.$$

$$\underset{\text{Sulphur trioxide.}}{SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

$$\underset{\text{Phosphorous pentoxide.}}{P_2O_5} + H_2O = \underset{\text{Metaphosphoric acid.}}{2\,HPO_3}.$$

$$\underset{\text{Carbon dioxide.}}{CO_2} + H_2O = \underset{\text{Carbonic acid.}}{H_2CO_3}.$$

$$\underset{\text{Nitrogen pentoxide.}}{N_2O_5} + H_2O = \underset{\text{Nitric acid.}}{2\,HNO_3}.$$

Certain metallic oxides are, however, acidic, *e.g.* chromium trioxide, CrO_3, and manganese heptoxide, Mn_2O_7.

(2) *Basic Oxides.*—These are the oxides of the metals which on treatment with acids yield salts and water *only* (cf. peroxides). A few of them are soluble in water, combining with it to form hydroxides. Such are potassium monoxide, K_2O, calcium monoxide or quick-lime, CaO, and barium monoxide, BaO. With water these form, respectively, potassium hydroxide or caustic potash, KOH, calcium hydroxide or slaked lime $Ca(OH)_2$, and barium hydroxide, $Ba(OH)_2$.

$$K_2O + H_2O = 2\,KOH.$$

$$CaO + H_2O = Ca(OH)_2.$$

$$BaO + H_2O = Ba(OH)_2.$$

The majority of the metallic oxides are, however, insoluble in water, and their hydroxides can only be obtained indirectly.

Oxides which are both Acidic and Basic.—There are some oxides which at one time play the part of basic oxides and at another of acidic oxides, and it is only by considering the nature of the salt in which they occur that we can say in which capacity they are acting. Such oxides are called *amphoteric*. For instance, sodium stannate, Na_2SnO_3, is formed from soda and oxide of tin, the oxide of tin being the acid constituent, whilst in stannic sulphate, $Sn(SO_4)_2$, the oxide of tin is the basic constituent.

Similarly aluminium oxide dissolves in acids to form a salt of aluminium—

$$Al_2O_3 + 6\ HCl = 2\ AlCl_3 + 3\ H_2O.$$

It also dissolves in a solution of caustic soda to give sodium aluminate.

$$Al_2O_3{\cdot}3H_2O + 2\ NaOH = 2\ NaAlO_2 + 4\ H_2O.$$

(3) *Peroxides.*—These are oxides which contain a high percentage of oxygen and do not form corresponding salts with acids. They may be divided into two classes: (1) those which form hydrogen peroxide with dilute mineral acids; (2) those which do not. Examples of Class (1) are barium peroxide, BaO_2, and sodium peroxide, Na_2O_2; and of Class (2) manganese dioxide, MnO_2, and lead peroxide, PbO_2. All peroxides on heating with strong sulphuric acid evolve oxygen and form sulphates corresponding to a lower oxide of the metal. Thus barium peroxide forms barium sulphate corresponding to BaO, and lead peroxide forms lead sulphate corresponding to PbO.

$$2\ BaO_2 + 2\ H_2SO_4 = 2\ BaSO_4 + 2\ H_2O + O_2.$$

$$2\ PbO_2 + 2\ H_2SO_4 = 2\ PbSO_4 + 2\ H_2O + O_2.$$

Exp. 26. Heat gently small quantities of barium peroxide and lead peroxide with strong sulphuric acid in test-tubes, and test the evolved gas for oxygen.

A peroxide belonging to Class (2) evolves *chlorine* on heating with strong hydrochloric acid, and is converted into the chloride corresponding to a lower oxide;

$$e.g.\ PbO_2 + 4\ HCl = PbCl_2 + 2\ H_2O + Cl_2.$$

One belonging to Class (1), on the other hand, yields *oxygen* or *chlorine* and the chloride derived from a lower oxide on similar treatment;

$$e.g.\ 2\ Na_2O_2 + 4\ HCl = 4\ NaCl + 2\ H_2O + O_2$$

(4) *Suboxides and Neutral Oxides.*—Suboxides contain less oxygen than the normal oxide, *e.g.* C_3O_2 carbon suboxide, Ag_4O silver suboxide, Cu_4O copper suboxide.

Neutral oxides are oxides—nitric oxide, NO, carbon

monoxide, CO, nitrous oxide N_2O—which cannot be placed in any of the classes mentioned above.

100. Proof that Oxides Contain Oxygen.—The following method may be adopted to prove that oxides which do not evolve oxygen on heating, and are not reduced on heating in hydrogen (*e.g.* quicklime), contain oxygen :—

Exp. 27. Introduce a layer of quicklime (CaO) into a glass tube, and connect it with an apparatus for preparing dry hydrochloric acid. On heating the quicklime and passing dry hydrochloric acid, water is formed, thus proving that quicklime contains oxygen, for we know that dry hydrochloric acid does not, since it is produced by the direct combination of the elements hydrogen and chlorine.

101. Liquid Oxygen.—Almost simultaneously two French chemists, Pictet and Cailletet, succeeded independently in reducing oxygen to the liquid state in the year 1877. The methods used by these two experimenters differed in principle. Pictet cooled the gas to a temperature of — 140° C. (which is below its critical temperature), and then submitted it to great pressure. Cailletet allowed oxygen at a pressure of 300 atmospheres to suddenly expand against external pressure; the heat absorbed during the expansion (which was the equivalent of the work done against the external pressure) was so great that the temperature of the gas fell to its point of liquefaction.

More recently a method has been devised by Linde and Hampson (independently) which enables liquid oxygen to be obtained from air in large quantity. This method, which differs in principle from those of both Pictet and Cailletet, is used to liquefy air, and is described under "liquid air." To obtain oxygen from liquid air use is made of the fact that nitrogen boils at a lower temperature than oxygen. If, therefore, the liquid is allowed to boil away, the nitrogen passes off first, and liquid oxygen remains behind in a state of comparative purity (see § 237).

Liquid oxygen is a light blue substance boiling at — 181° C., at which temperature its specific gravity is 1·135 (water = 1). It possesses strongly magnetic properties, and is a very perfect non-conductor of electricity.

As might be expected, oxygen loses a great deal of its chemical activity when reduced to the liquid state. Such substances as sodium, potassium, and phosphorus are not acted upon when immersed in liquid oxygen.

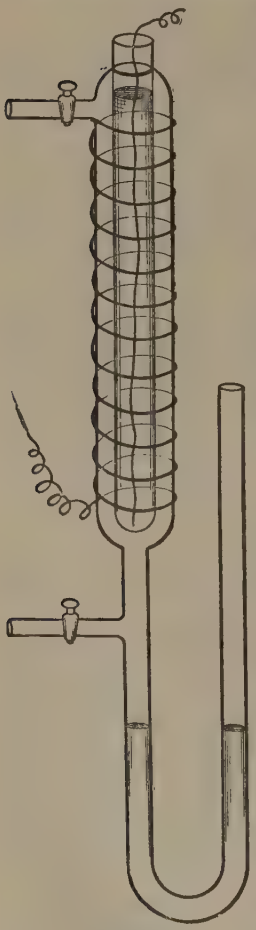


Fig. 16.

Ozone, O_3.

102. Ozone. Formation and Preparation.—Von Marum observed in 1785 that when electrical discharges took place in air or oxygen a special odour developed. Many years later Schönbein, in 1840, discovered the reason; he called the substance that was formed and gave this odour, ozone (Greek *ozo*, I smell). He also prepared ozone in several ways.

Formation of Ozone. — Ozone is formed during the electrolysis of water, by the slow oxidation of phosphorus, and when hydrogen peroxide is decomposed. By the action of free fluorine on water, and by the electrolysis of sulphuric acid small quantities of ozone are produced.

Preparation of Ozonised Oxygen.— Ozone can be conveniently obtained by passing a "silent discharge" from two Grove's cells and an induction coil, through dry oxygen. For this purpose the apparatus shown in Fig. 16 may be used. An outer tube AB ending below in a narrower portion bent into a U-tube, is provided with two stopcocks, and an inner tube of somewhat smaller diameter, closed at the bottom, and sealed

in at A. The outer tube is surrounded throughout its whole length by a coil of platinum wire, and the inner tube is filled with dilute sulphuric acid, and another platinum wire dips into this.

The stopcocks are opened, and concentrated sulphuric acid is poured into the U-tube, which serves as a gauge, and dry oxygen passed through the annular space till the air is swept out. The stopcocks are now closed and the two platinum wires connected to the terminals of the induction coil. The temperature of the apparatus should be kept constant during the experiment, and this may easily be effected by surrounding it with water at the same temperature as the room. After passing the current for a little while some of the oxygen contained in the space between the tubes will have been converted into ozone.

It will be observed that the volume of the gas in the annular space diminishes, as will be indicated by the sulphuric acid in the gauge. By determining beforehand the relative volume of the space in which the oxygen is confined, and that of a given length of the U-tube, an approximate estimate may be made of the amount of contraction.

By using this method not more than 8 to 10 per cent. of the oxygen can be transformed into ozone. Other methods have been tried which give a greater yield. Oxygen containing 23 to 28 per cent. ozone is obtained by electrolysing sulphuric acid under special conditions. Ozone is easily formed by passing the electric arc through liquid oxygen.

103. Properties and Uses.—The properties of ozone may be demonstrated by using the apparatus shown in Fig. 16—

(1) Attach a tube at the upper stopcock, open both stopcocks, and drive out some of the ozonised oxygen at the lower one, holding a paper dipped in solution of potassium iodide near the outlet. The paper will turn brown from the liberation of iodine, the ozone being transformed into ordinary oxygen.

$$2\,KI + O_3 + H_2O = 2\,KOH + O_2 + I_2.$$

(2) Bleach indigo or moist litmus in a similar way.

(3) Note the odour of the ozone.

(4) Put a globule or two of mercury in a small flask and pass ozonised oxygen into the flask. On shaking, the mercury is superficially oxidised, loses its convexity of surface, and spreads out in a film on the walls of the flask.

(5) Expel the ozonised oxygen from the lower stopcock through a glass tube about 20 cm. long, heating the tube to dull redness; at 250° C. ozone is transformed into oxygen, and after heating, a test made as in (1) should give no liberation of iodine.

The above observations show the great chemical activity of ozone, and the features by which it is distinguished from oxygen, for ordinary oxygen does not bleach, nor does it oxidise mercury or liberate iodine from potassium iodide at ordinary temperatures.

Ozone is a relatively stable gas which decomposes slowly at the ordinary temperature, and rapidly at 400° C. It is slightly soluble in water and combines with certain essential oils, especially with oil of turpentine, and cinnamon oil. Silver and lead are converted by it to the peroxides.

Ozone is an endothermic substance requiring 32,208 calories for the formation of one gramme molecule, and it can therefore be easily understood that it has a greater oxidising power than oxygen, and that it is unstable.

Ozone readily attacks rubber tubing, and rubber connections should therefore be avoided in making experiments with the gas. When ozonised oxygen is passed through a tube surrounded by liquid oxygen the ozone condenses to a blue liquid, which boils at — 119° C. with formation of a blue explosive gas. Liquid ozone, like liquid oxygen, is magnetic.

Uses of Ozone.—Ozone has been used to sterilise water. The enclosed air in theatres, etc., and underground compartments is greatly deodorised and improved by the use of ozonised air. It is used in organic chemistry and for the preparation of vanillin.*

*Vanillin is C_6H_3 (CHO) (OCH_3) (OH), and is used for flavouring foods.

104. Composition of Ozone.—Ladenburg, using a mixture containing 86·16 of ozone, has shown that the density of pure ozone is 24 (H = 1). Its molecular weight, therefore, is $2 \times 24 = 48$. Now since the atomic weight of oxygen is 16, a molecule of ozone must consist of three atoms of oxygen, for $3 \times 16 = 48$. This explains why there is a diminution of volume when oxygen is converted into ozone, for *three* molecules of oxygen (O_2) give rise to only *two* molecules of ozone (O_3)—

$$3\ O_2 = 2\ O_3.$$

Applying Avogadro's hypothesis, it follows that three volumes of oxygen should give rise to two volumes of ozone. This may be proved experimentally in the following manner :—

The contraction in volume on ozonising a known volume of oxygen is measured. The ozone is then absorbed by turpentine, and the further diminution in volume noted. Thus suppose in an experiment 100 vol. of oxygen contracted to 97 vol. on being ozonised, and absorption with turpentine caused a further diminution of volume to 91 vol. Then we have—

Volume of ozone ... ... = (97−91 vol.) = 6 vol
,, ,, oxygen from which it was formed = (100−91 vol.) = 9 vol.

The ozone was therefore formed by the condensation of 9 vol. of oxygen into the space of 6 vol., or 3 vol. of oxygen condense to produce 2 vol. of ozone.

Soret adopted a method of measuring the density of ozone which consisted in comparing the rate of diffusion of ozonised oxygen with that of other gases. For example, he compared the rates of diffusion of ozonised oxygen and chlorine respectively into pure oxygen. He next estimated the percentage of ozone in the ozonised oxygen, and from this was able to calculate the relative rate of diffusion of ozone and chlorine, which worked out at approximately 6 : 5. Now applying Graham's Law (see § 33) we have—

$$\frac{\text{Rate of diffusion of ozone}}{\text{Rate of diffusion of chlorine}} = \frac{\sqrt{\text{Density of chlorine}}}{\sqrt{\text{Density of ozone}}}.$$

The density of chlorine is 35·4 ;

$$\therefore \quad \frac{6}{5} = \frac{\sqrt{35{\cdot}4}}{\sqrt{\text{Density of ozone}}},$$

$$i.e. \quad \frac{36}{25} = \frac{35{\cdot}4}{\text{Density of ozone}};$$

$$\therefore \quad \text{Density of ozone} = \frac{35{\cdot}4 \times 25}{36} = 24{\cdot}6 \text{ (approx.)}.$$

This is in approximate agreement with the value determined directly.

Further, if mercury is placed in contact with ozone the metal is oxidised at the expense of an atom of oxygen from the ozone. Oxygen remains, and there is no change of volume.

105. Allotropy.—Oxygen and ozone afford the first example of a phenomenon exhibited by several elements, namely, of existing in two or more forms with different physical and to some extent chemical properties. The less common forms are said to be **allotropic modifications** of the commonest ; thus ozone is an allotropic modification of oxygen.

When one allotropic modification of an element is converted into another, heat is invariably either evolved or absorbed ; if there are two modifications of an element A and B, and if heat is evolved when A is converted into B, it will be absorbed when B is converted into A.

Now oxygen is changed into ozone with absorption of heat. It is a general rule that bodies produced with absorption of heat possess more internal energy and are decomposed very easily, giving out the heat absorbed in their formation. This explains the greater activity of ozone as compared with oxygen. The molecule of ozone readily breaks down into a molecule of oxygen and a free atom of oxygen, with evolution of heat—

$$O_3 = O_2 + O.$$

This free atom of oxygen immediately attacks any oxidisable substance within reach, such as mercury, potassium iodide, etc., and if no such substance is present the free oxygen atoms unite to form stable molecules of oxygen.

The reason that a free atom of oxygen is so much more active than a molecule of oxygen is that before the latter can enter into a chemical reaction it must be broken down into two atoms of oxygen, and it requires the expenditure of a considerable amount of energy to bring this about.

106. Nascent State.—An element when just liberated from a compound is said to be **nascent** (Latin, *nascor*, I am born), and in general it shows special activity when in this state. This will be understood from what has just been said with regard to oxygen, for an element is always in the atomic condition when just set free from combination.

Another example of the greater activity of an element in the nascent state is afforded by the following experiment with hydrogen.

Exp. 28. Prepare hydrogen by the action of granulated zinc on dilute sulphuric acid and convey it by means of a delivery tube into a beaker containing a solution of potassium permanganate (pink). Introduce some of the permanganate into a second beaker and add dilute sulphuric acid and zinc. Note that in the latter case the colour of the permanganate gradually disappears, whereas in the former case it remains unchanged.

The explanation is that when the hydrogen is produced *in contact with* the potassium permanganate, as in the second case, it is in the *nascent state* (H) and reduces the permanganate in presence of sulphuric acid with formation of manganous sulphate, which is practically colourless in dilute solution.

$$\underset{}{Zn} + \underset{}{H_2SO_4} = \underset{}{ZnSO_4} + \underset{\text{Nascent.}}{2\,H}$$

$$\underset{\text{Potassium permanganate.}}{2\,KMnO_4} + 3\,H_2SO_4 + \underset{\text{Nascent.}}{10\,H} = K_2SO_4 + \underset{\text{Manganous sulphate.}}{2\,MnSO_4} + 8\,H_2O.$$

When, on the other hand, the hydrogen is produced *externally* and then passed into the permanganate solution, as in the first case, it is in the *molecular state* (H_2) and exercises no reducing action.

QUESTIONS.—CHAPTER XII.

1. Write a short account of the *phlogiston theory.*

2. Describe a laboratory method of preparing oxygen, and sketch the apparatus used.

3. What explanation has been advanced of the action of manganese dioxide in the preparation of oxygen from potassium chlorate ?

4. Give a list of oxides which evolve oxygen on heating, and represent the decompositions which they undergo by equations.

5. Express by equations the changes which take place when the following substances are heated : (1) a mixture of manganese dioxide and strong sulphuric acid, (2) potassium nitrate, (3) a mixture of potassium permanganate and strong sulphuric acid.

6. How may oxygen be obtained from bleaching powder ?

7. How is oxygen prepared commercially ?

8. Give instances of the formation of oxides by the action of oxygen on elementary substances, (*a*) where such action takes place at ordinary temperatures, (*b*) where heat must be applied in order to start the reaction.

9. What takes place when the products of combustion of carbon, sulphur, and phosphorus are respectively brought into contact with water ?

10. What is meant by *slow combustion*

11. Explain the term *oxidising agent.*

12. What is an *oxide* ? Give instances of oxides of the metals which are soluble in water, and of oxides which are insoluble in water.

13. How do acid-forming oxides (anhydrides) differ from basic oxides ? What is usually the effect of bringing together solutions of these two classes of oxides ?

14. Explain the term amphoteric oxide, giving examples.

15. How may ozonised oxygen be distinguished from ordinary oxygen (*a*) without the application of reagents, (*b*) by means of chemical tests ?

16. What experiments indicate that ozone is a more active oxidising agent than oxygen ?

CHAPTER XIII.

COMPOUNDS OF HYDROGEN AND OXYGEN.

107. The Two Compounds.—Hydrogen and oxygen combine together in two proportions, forming water, H_2O, and hydrogen peroxide, H_2O_2; the latter contains twice as much oxygen in relation to hydrogen as the former.

Water, H_2O.

We shall commence the study of water by investigating its composition by volume and by weight.

108. Composition of Water by Volume.—As already stated, it was Cavendish who first proved the composition of water. He introduced a mixture of two volumes of hydrogen and one of oxygen into a strong glass vessel fitted with two wires which passed into the inside of the vessel so as nearly to touch one another. The electric spark was passed by means of the wires, and the gases exploded. By repeating the experiment many times he was able to show that oxygen combines with twice its volume of hydrogen and that the liquid resulting from the combination was water.

The method employed in the laboratory to prove the volumetric composition of water is similar in principle to that employed by Cavendish but capable of greater accuracy, and moreover it is applicable to gases in general; it was first introduced by Bunsen.

A tube of even bore, A, about 70 cm. in length. is used. This is furnished with platinum wires, E, to enable the gases to be "sparked," and millimetre divisions are etched on the tube. The "eudiometer," as such a tube is called, is first calibrated so that its relative volume down to any given graduation is known. It is then filled with mercury (see

Fig. 17) by adjusting the levelling tube B and opening the stopcock C.

Pure oxygen sufficient to occupy about one-tenth of the volume of the eudiometer is now passed in, and the exact volume is obtained by bringing the mercury to the same level in the eudiometer and the levelling tube. Hydrogen is then added equal to about six or seven times the volume of the oxygen, and the volume again read. The temperature and pressure existing at the time must also be noted. The levelling tube is now depressed so that the mercury falls nearly to the bottom of the eudiometer tube, and a spark is passed by connecting the platinum wires with a battery and an induction coil.

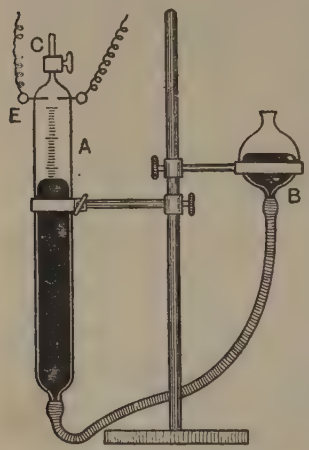


Fig. 17.

Under these circumstances the whole of the oxygen enters into combination with hydrogen, and as the water which forms condenses a partial vacuum is formed inside the tube, and on gently raising the levelling tube the mercury is seen to rise. After allowing sufficient time for the gas to regain the temperature of the room (much heat having been generated by the combination which has taken place) the level of the mercury in the eudiometer is again adjusted, and the volume of residual gas is read.

We have now the whole of the data necessary for ascertaining the relative volumes of hydrogen and oxygen which have united to form water. The volumes occupied by the gases are all reduced so as to represent standard conditions. When this has been done, let us suppose—

Oxygen taken occupied	12	volumes.
Hydrogen added	,,	80	,,
Residual hydrogen	,,	56	,,

It is evident that 12 volumes of oxygen have entered into combination with $80 - 56 = 24$ volumes of hydrogen to form water.

The above method of finding the volumetric composition of water is a *synthetic* method. An *analytical* method consists in the electrolysis of acidulated water when two volumes of hydrogen to one of oxygen are obtained.

109. Correction for Pressure of Aqueous Vapour.—There is one correction in the above description which has been omitted. A small quantity of water vapour is produced on the combination of hydrogen and oxygen, and this vapour exerts a pressure so that the pressure exerted by the residual hydrogen is rather less than that measured as above, which is the total pressure of hydrogen plus water vapour. The amount of water vapour produced is however too small to *saturate* the residual hydrogen, so the vapour pressure is not known. How then are we to make the necessary correction?

The method adopted is to ensure that the residual gas is saturated with aqueous vapour by moistening the eudiometer with a few drops of water before introducing the mercury at the commencement of the experiment. Of course, all the other volumes of gas measured will also be saturated with aqueous vapour, and the pressure which it exerts can be found by noting the temperature of the gas and referring to the tables. If, then, the pressure of any of the volumes of gas as previously measured was found to be P and the saturation pressure of water vapour at the temperature of the gas is p, then the corrected pressure is $P - p$.

110. Volumetric Composition of Steam.—In order to find the relation between the volumes of hydrogen and oxygen which combine, and that of the steam produced from them, we must so arrange the experiment that the temperature of the gas is maintained above the boiling-point of water. The steam produced will not, under these conditions, condense to water.

The apparatus shown in Fig. 18 may conveniently be used for this experiment. A is a eudiometer as used in § 108. The tube is filled with mercury and surrounded by a wider tube, F, through which the vapour of a liquid boiling at about 130° C. (*e.g.* amyl alcohol) is passed by means of D.

A mixture of hydrogen and oxygen in the proportion of 2 : 1 by volume (obtained by the electrolysis of water) is now passed into the eudiometer by depressing the levelling tube B and opening the stopcock C. When the explosion tube is about two-thirds full of gas the supply is cut off and the mixture is allowed to attain the temperature of the jacket.

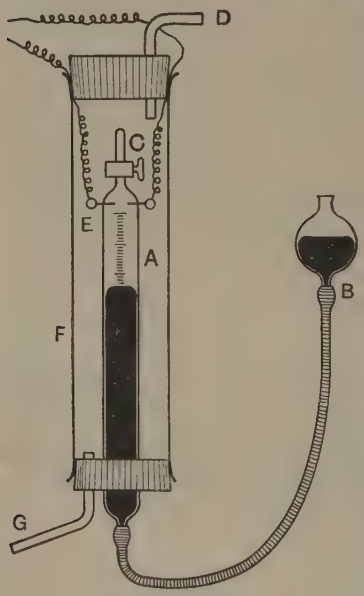


Fig. 18.

The volume of the mixed gases is then read by adjusting the level of mercury in the eudiometer.

The levelling tube is then depressed until the mercury falls nearly to the bottom of A and the gases are sparked as in § 108. The gases combine, and on bringing the mercury in A and B to the same level, it will be seen that the volume of steam occupies two-thirds that of the mixed gases. On cooling down to the ordinary temperature, the mercury will rise almost to the top of A if B is raised—not quite owing to the small vapour pressure which water exerts at ordinary temperature ; this shows that there is no hydrogen or oxygen remaining uncombined.

From this experiment it follows that steam contains its own volume of hydrogen and half its volume of oxygen, which agrees with the equation—

$$2\,H_2 + O_2 = 2\,H_2O.$$
$$4\text{ vol.} \quad 2\text{ vol.} \quad 4\text{ vol.}$$

111. Composition of Water by Weight.—Many oxides, such as those of lead, copper, iron, etc., when heated in a current

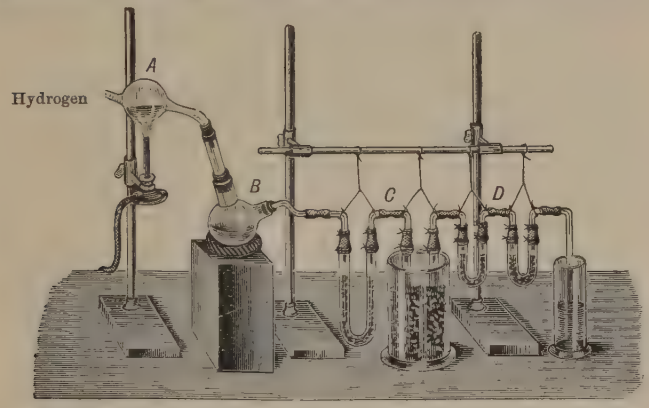


Fig. 19.

of hydrogen give up their oxygen, and are "reduced," as it is termed, to the metallic condition. In this reduction the oxygen combines with hydrogen with the production of water.

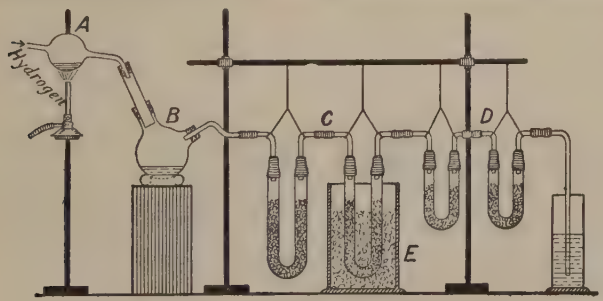


Fig. 20.

If, then, we can ascertain (1) the weight of the water formed, and (2) the weight of the oxygen which has gone to form it, we shall have by difference the weight of the hydrogen contained

in the water, and thus a full synthesis of water by weight. Very careful experiments have been performed in this way, using oxide of copper (CuO) as the medium for the supply of the oxygen. The equation expressing the reaction is—

$$CuO + H_2 = Cu + H_2O.$$

Our requirements for performing the synthesis are—

(1) Pure hydrogen.

(2) A known weight of oxide of copper.

(3) A means of collecting and weighing the *whole* of the water produced.

Dumas and Stas, in 1843, performed the synthesis of water in this way with extreme care, and the requirements above mentioned were attained in the following manner. The hydrogen, prepared by the action of zinc on sulphuric acid, was purified as described in § 78. The oxide of copper was placed in a bulb A (Fig. 19),* the weight of both being determined. The greater part of the water condensed in the bulb B, and the rest was absorbed in U-tubes containing solid caustic potash C and phosphorus pentoxide D.

Weighings before and after the experiment show—

(*a*) The loss of weight of the oxide of copper, that is the amount of oxygen used;

(*b*) The gain in weight of the second bulb B and the U-tubes succeeding it, that is the amount of water formed. As the

* In sketching apparatus the student is advised not to attempt *perspective* drawings which take a long time and are seldom satisfactory. A much better plan is to draw the apparatus *in front elevation, i.e.* as it would be seen by a person looking at it straight in front. When, however, the exact nature of any part of the apparatus can be better explained by drawing it *in section, i.e.* as if it were cut in two through the middle and the front half removed, this method should be adopted for that particular part.

To indicate that an object has been cut through, inclined lines are drawn parallel to one another across any part which is sufficiently thick for its two sides to be represented by separate lines (thin glass vessels, for instance, do not admit of this). Fig. 20 is a drawing, partly in front elevation and partly in section, of the apparatus shown in perspective in Fig. 19. For instance, the retort-stands are represented in front elevation in Fig. 20, whilst the vessels B and E are drawn in section.

combined result of nineteen determinations, they found that the amount of oxygen used was 840·161 grm. and the amount of water formed 945·439 grm. Water consists, therefore, of

840·161 grm. of oxygen
and 105·278 „ „ hydrogen;

or one part by weight of hydrogen combines with 7·98 parts by weight of oxygen to form water.

More accurate experiments performed by E. W. Morley in 1895 are described below.

112. Morley's Experiments.—Morley investigated the composition of water in two ways—

(*a*) By finding the ratio of the combining volumes of hydrogen and oxygen.

(*b*) By determining the weight of water produced by the combination of known weights of hydrogen and oxygen.

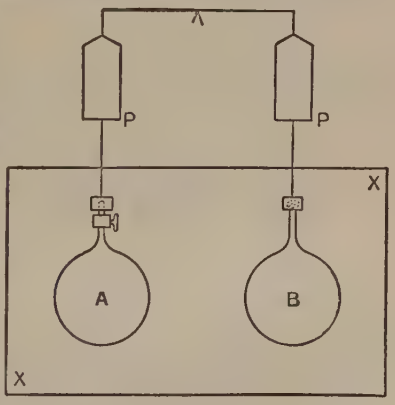


Fig. 21.

(*a*) In the first method the oxygen (prepared by heating potassium chlorate or by the electrolysis of dilute sulphuric acid) was weighed *directly*, using globes of 20 litres capacity. These globes (Fig. 21), were suspended from the pans of a balance and were enclosed in a large desiccator cupboard in pairs, one to each balance pan. All the necessary corrections were made for temperature and pressure, and the mean of several experiments taken. The value for the density of oxygen was found to be 1·42900 ± ·000034.

This method was not used to find the density of hydrogen for the following reasons: (1) The weight of the globe was 600 times heavier than the hydrogen, (ii) the risk that the

small weight of the hydrogen might be appreciably increased by the presence of mercury vapour. Morley therefore used another method, in which hydrogen was weighed in a tube containing 600 grm. of palladium (Fig. 22). This metal absorbed 3·8 grm. of hydrogen, and on heating evolved about 40 litres of pure hydrogen, *i.e.* about 3·7 grm. which was collected in large globes of known volume immersed in ice. The pressure produced in the globes was measured, and knowing the weight and the volume of the gas, Morley determined the density. He found that the average of twenty-five experiments gave the value—

$$\text{Density of hydrogen} = 0{\cdot}089873 \pm 0{\cdot}0000027.$$

Morley then found the ratio of the combining volumes of hydrogen and oxygen, and hence the weights of the two gases which combine. To do this he electrolysed a dilute solution of caustic potash, determined the density of the gas produced as above, and then calculated the proportion of hydrogen to oxygen. The gases were then exploded and a slight excess of hydrogen was found. After correcting for this, Morley found that the combining volumes were in the proportion 2·00269 of hydrogen to 1 of oxygen. Thus these values combined with the values of the densities found gave the ratio of the weights as—

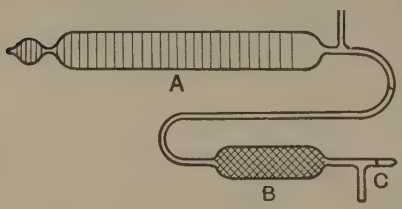


Fig. 22.

$$\text{Oxygen} : \text{Hydrogen} = 7{\cdot}9395 : 1,$$

(*b*) For a second method of determining the composition of water, Morley then used a special apparatus to find the weight of water produced from known weights of hydrogen and oxygen. The hydrogen and oxygen used were obtained as described above.

Two platinum wires, *F F* (Fig. 23), for sparking passed through a chamber *A B*, which was fitted with two drying tubes, *C* and

D, containing phosphorus pentoxide to prevent loss of water formed during the reaction. After evacuation and weighing pure dry hydrogen and pure dry oxygen were allowed to enter through *EE*, and were ignited by the sparks from *FF*, the water formed collecting in *B*. The rates at which hydrogen and oxygen entered were regulated by the taps *C* and *D*, etc., so that the formation of water was continuous.

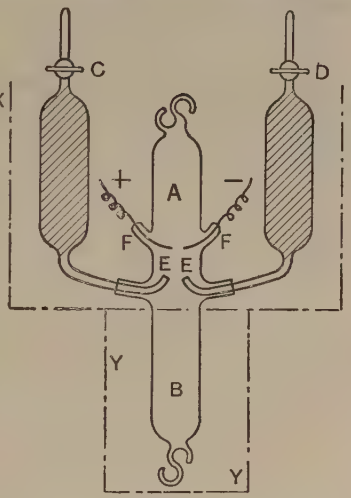


Fig. 23.

The whole apparatus was kept cool; *XX* being a jacket of cold water, *YY* a freezing mixture. When a suitable weight of the gases had thus reacted the unconsumed hydrogen and oxygen remaining in the tube were pumped out and analysed and the apparatus and water weighed. The weights of hydrogen and oxygen used, and the weight of water formed were known, and Morley found the following ratios, as the mean of twelve experiments—

(i) Water to hydrogen = 8·9392 : 1
or oxygen to hydrogen = 7·9392 : 1

(ii) Oxygen to hydrogen = 7·9396 : 1.

Comparing these results with the result of (*a*), which gives 7·9395 : 1, we may take the general mean as—

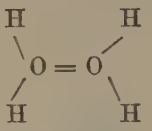
Oxygen : Hydrogen = 7·9394 : 1.

113. Composition of the Water Molecule.—These experiments show that water has the percentage composition represented by the formula H_2O. However, the *molecular*

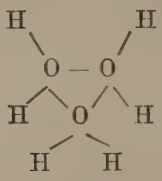
composition of liquid water although assumed to be H_2O is really much more complex, and consists of an equilibrium mixture of H_2O "hydrol," $(H_2O)_2$ "dihydrol," and $(H_2O)_3$ "trihydrol." Ice also exists in several forms, *e.g.* light ice (probably H_6O_3), and dense ice (probably H_4O_2). The vapour density of steam at temperatures well above 100° corresponds to H_2O, but increases about the boiling point probably owing to the formation of molecules such as H_4O_2.

These forms of water can be represented graphically as follows :—

(*a*) *Hydrol.*



(*b*) *Dihydrol.*



(*c*) *Trihydrol.*

It will be readily seen that in (*b*) and (*c*) oxygen is tetravalent, an assumption which is supported by considerable independent evidence.

114. Physical Properties of Water.—When pure, water is a clear and tasteless liquid ; under ordinary circumstances it may be regarded as colourless, but in reality it has a faintly bluish tinge which is perceptible when white light is passed through a stratum of about 20 ft. in thickness.

At atmospheric pressure (760 mm.) water boils at 100° C. and freezes at 0° C., and these are used as the two principal fixed points on the thermometric scale. The density of water is unity, that is at 4° C. one cubic centimetre weighs one gramme ; also a fixed standard. Water contracts from 0° C.

to 4°, and then expands. Also in thawing, ice expands, a fact which accounts for burst pipes in frosty weather.

The amount of heat required to raise the temperature of one gramme of water through 1° C. is called the *calorie*, and is the unit of heat. The specific heat of water is also unity.

115. Chemical Properties of Water.—Pure water is tasteless and odourless. Most of the solid substances and gases which we meet with in chemical operations dissolve to an appreciable extent in water; some liquids, such as alcohol and sulphuric acid, associate themselves with water in all proportions; whilst others, such as oils, if shaken up with water separate again, being taken up by the water either only to a slight extent or not at all. Water is an ionising solvent, that is, solutions of acids, bases, and salts are electrolytes.

Pure water is practically a non-conductor of electricity, and is decomposed by heat (§ 77). Many metals decompose water either at the ordinary temperature or when heated (§ 77). The decomposition of phosphorus trichloride by the addition of water,

$$PCl_3 + H_2O = POCl + 2\,HCl,$$

is an example of hydrolysis. Many examples of hydrolysis or decomposition by the addition of water will be found later in this book. Water is very active as a catalyst, in causing certain chemical changes which do not take place in perfectly dry materials, *e.g.* the dissociation of ammonium chloride (see *Inorganic Chemistry, Mainly Metals*).

Water possesses the power of combining directly with a very great many substances. Sometimes the compounds are very easily broken up again, whilst in other cases they are remarkably stable (see §§ 118-19).

116. Solubility of Solids.—The extent to which solid substances are soluble in water under similar circumstances varies according to the nature of the substance.

Minerals, such as coal, limestone, quartz, and some chemical compounds, such as sulphate of lime, oxide of lead, sulphide of iron, are only very slightly soluble, whilst others, *e.g.* nearly

all chlorides and nitrates, are freely soluble. In any case, however, there is a limit to the amount of solid matter which can be dissolved, and when water has taken up as much as it will, we have what is known as a *saturated* solution.

The quantity of a substance required to form a saturated solution is usually greater the higher the temperature, though there is no simple general relation between the temperature and the amount dissolved.

The solubility in parts per 100 of water is given for a few substances in the following table—

	0° C.	20° C.	50° C.	100° C.
Potassium nitrate ...	13·3	31·2	85·0	246·0
Sodium chloride ...	35·5	36·0	37·0	39·6
Potassium chlorate ...	3·3	8·0	19·0	58·0
Sodium chlorate ...	81·9	99·0	136·0	232·6
Mercuric chloride ...	5·7	7·4	11·3	54·0
Potassium sulphate ...	8·3	12·5	17·0	26·0

	0° C.
(*a*) Barium sulphate	·0023
(*b*) Silver chloride	·0018
(*c*) Calcium carbonate	·001

The last three substances (*a*), (*b*), and (*c*) are given to show how "insoluble" substances even dissolve to a very small extent.

117. Solubility Curves.—Let us now investigate the solubility of nitre quantitatively at different temperatures.

Exp. 29. Introduce about 100 c.cm. of water into a small flask, add some finely powdered* nitre, and shake well. If the powder all dissolves add more and shake again. Repeat the addition of nitre, if necessary, till some remains undissolved after vigorous shaking, *i.e.* the solution is *saturated*. Allow the mixture to settle, take the temperature of the liquid with a thermometer (say 10° C.), and then pour off about 10 c.cm. of the clear liquid into a weighed porcelain dish, after carefully wiping the inside of the neck of the flask, on which there may be some solid nitre, or water unsaturated with nitre. Weigh again. The difference gives the weight of the solution (*w* grm., say).

* Solution takes place more rapidly and effectively if the substance is finely powdered.

Now evaporate to dryness on the water bath, wipe the moisture off the bottom of the dish, and weigh. The difference between this and the weight of the empty basin gives the weight of nitre dissolved. Suppose this is w_1 grm., then we have w_1 grm. of nitre dissolved in $w - w_1$ grm. of water. Therefore at 10° C. the weight of nitre which would dissolve in 100 grm. of water would be $\frac{w_1}{w - w_1} \times 100$ grm. This is the *solubility of nitre at* 10° *C. expressed as a percentage.*

Now warm the water in the flask to about 20° C. and find the solubility as before. Repeat at 30°, 40°, and 50° C.

Next take a piece of squared paper and draw two lines (axes) at right angles, one horizontal along the bottom of the paper, the other vertical along the left-hand side. Mark off along the horizontal axis lengths proportional to the temperatures taken, and on the vertical axis lengths proportional to the solubilities. Now from each point representing a solubility draw a horizontal line till it cuts a vertical line from the corresponding temperature. Make a cross at the point of intersection. Join the centres of the crosses by a line, drawing the line so that it forms a smooth curve (see Fig. 24). This is called the *solubility curve* of nitre.

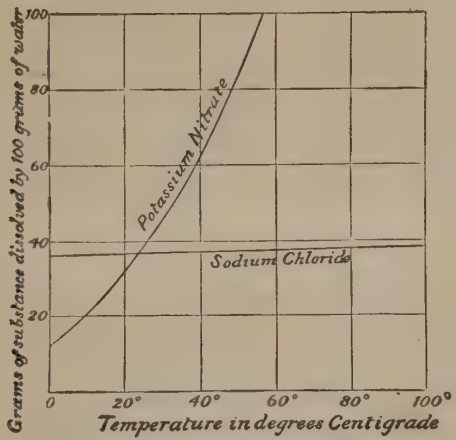


Fig. 24.

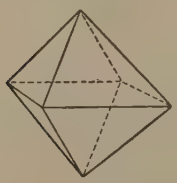
By means of this curve we can at once find the solubility of nitre at any temperature between 0° C. and 50° C. All we have to do is to follow the vertical line corresponding to the required temperature till it cuts the curve; then follow

the horizontal line from this point till it cuts the vertical axis and read off the solubility.

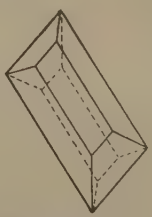
118. Water of Crystallisation.—Many salts, when they are allowed to crystallise from solution, contain water, which is associated with them in definite proportions, and it cannot be regarded otherwise than as water *in combination* with the salt.

There is, however, very little stability in the combination; for instance, copper sulphate crystallises with the composition $CuSO_4 + 5\ H_2O$. At 100° C. $4\ H_2O$ is set free, and the remaining molecule of water requires a temperature of 240° C. to liberate it.

Alum crystallises with $24\ H_2O$; $10\ H_2O$ separate at 100° C., a further $9\ H_2O$ at 120° C., and nearly the whole of the remainder at 280° C. In some cases, indeed, such as crystallised sodium carbonate or washing soda, $Na_2CO_3 + 10\ H_2O$, the salt loses water or *effloresces* at ordinary temperatures in a dry atmosphere.



Alum.
$K_2SO_4.Al_2(SO_4)_3.24H_2O$.
Fig. 25.



Washing soda.
$Na_2CO_3.10\ H_2O$.
Fig. 26.

Epsom salts.
$MgSO_4.7\ H_2O$.
Fig. 27.

The amount of water of crystallisation which attaches itself to a salt varies according to the temperature at which the crystals form. Thus, from a solution of sodium sulphate, crystals of $Na_2SO_4 + 7\ H_2O$ can be obtained at temperatures below 26°, or crystals of $Na_2SO_4 + 10\ H_2O$ (Glauber's salt) at temperatures below 34°; while above 34° crystals of Na_2SO_4 are obtained. Epsom salts, $MgSO_4 + 7\ H_2O$, furnishes another example, giving $MgSO_4 + 6\ H_2O$. Frequently, salts

which at ordinary temperatures separate from solution in the anhydrous condition, possess water of crystallisation when crystallised at low temperatures. Thus if a concentrated solution of common salt be allowed to stand at ordinary temperatures crystals of NaCl are obtained, but at — 10° C. crystals of $NaCl + 2\ H_2O$.

As examples of the crystalline forms assumed by salts containing water of crystallisation, we may consider three very common substances, viz. alum, washing soda, and Epsom salts. Figs. 25, 26, and 27 represent crystals of these substances, and it will be noticed how widely the three crystals differ in shape.

119. Compounds of Water with Oxides.—We have seen in discussing acids and bases that many oxides combine directly with water. The products vary in stability, but are as a whole very much more stable than those obtained when salts and water combine.

In many cases great heat is evolved when oxides and water unite, thus demonstrating the vigorous nature of the action.

Exp. 30. Pour a *little* water on to some quicklime contained in a porcelain dish. Note the clouds of steam formed, showing that much heat is evolved during the combination. Dip a thermometer in the mixture and note the rise of temperature.

Other examples of oxides which evolve much heat on combination with water are BaO, SO_3, P_2O_5. To bring about the decomposition of the compounds produced a correspondingly large amount of heat must be supplied, *i.e.* a high temperature is necessary.

To explain the greater stability of the compounds of water with oxides as compared with the compounds with salts, it is supposed that in the latter the water is present in *whole molecules* loosely combined with the molecule of the salt, whereas in the former it has completely lost its identity. Thus crystallised copper sulphate may be formulated $CuSO_4 + 5\ H_2O$ or $CuSO_4 \cdot 5\ H_2O$, but barium hydroxide must not be represented $BaO + H_2O$ or $BaO \cdot H_2O$, *i.e.* as containing a molecule of BaO and a molecule of water; it must be written

$Ba(OH)_2$, *i.e.* it contains two *hydroxyl* (OH) groups united to an atom of barium.

The constitutional formulae, adopting the two methods, will bring out the difference clearly—

(1) $Ba = O + H - O - H$

(2) $Ba \begin{matrix} O - H \\ O - H \end{matrix}$

It is supposed that all the compounds of water with oxides contain one or more (OH) groups, and they are consequently called *hydroxides*, whereas the combinations of salts and water are termed *hydrates*.

120. Action of Water on Compounds Containing Chlorine.—Many compounds of non-metals with chlorine, or chlorine and oxygen, react vigorously with water producing hydrochloric acid and another acid (or sometimes an oxychloride). Such substances are phosphorus trichloride, PCl_3, phosphorus pentachloride, PCl_5, phosphorus oxychloride, $POCl_3$, and sulphuryl dichloride, SO_2Cl_2. The phosphorus compounds react with water according to the following equations :—

$PCl_3 + 3\,H_2O = \underset{\text{Phosphorous acid.}}{H_3PO_3} + 3\,HCl.$

$PCl_5 + H_2O = POCl_3 + 2\,HCl$ (with a little water).

$POCl_3 + 3\,H_2O = \underset{\text{Phosphoric acid.}}{H_3PO_4} + 3\,HCl$ (with more water).

On combining the last two equations to represent the reaction of PCl_5 with excess of water we get—

$$PCl_5 + 4\,H_2O = H_3PO_4 + 5\,HCl.$$

The reaction between sulphuryl dichloride and water is represented thus—

$$SO_2Cl_2 + 2\,H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4} + 2\,HCl.$$

121. Natural Waters.—The water which evaporates from the surface of sea and land, and passes as water vapour into the air, is the purest form of natural water, and it retains its purity until it begins to fall as drops from the rain cloud.

Rain Water.—When this is collected at the surface of the earth it has passed through a considerable stratum of air, and dissolved in its passage not only gases normally occurring in the atmosphere, but also such impurities as are found there. Even then the solid matter contained in it does not amount normally to more than 3 or 4 parts per 100,000. In the neighbourhood of towns the impurities taken up are more numerous and in larger quantity; also near the sea, and especially during high winds, much sodium chloride is found in rain water.

River Water.—The composition of this water will of course depend on the nature of the surface and of the strata over which the water passes. For instance, a considerable part of the drainage area of the Thames consists of chalk, and its water contains about 30 parts of dissolved matter in 100,000, two-thirds of this consisting of calcium carbonate and sulphate, whilst the Dee in Scotland, passing over the older strata (principally slate and sandstone), contains about 5·6 parts of dissolved matter per 100,000, one-fourth of this being calcium salts. Since the water which passes into rivers collects from the surface of the soil, it contains also much more organic matter and carbon dioxide than rain water, arising from contact with plants and decaying vegetable matter.

Spring Water.—The water of springs is rain water which has percolated through soil and rocks. The composition of spring waters varies very considerably according to the depth from which the water rises and the nature of the strata which it has traversed. In some cases the amount of dissolved matter is very large, and such springs, especially when they have a saline taste or medical properties, are known as *mineral* springs.

The Springs of Bath and Harrogate contain magnesia and sulphuretted hydrogen, and are known as magnesia and sulphur waters; a spring near Woodhall Spa contains free iodine; many springs contain iron, and are known as *chalybeate* waters.

Mineral springs which rise from great depths are frequently hot, some having a temperature of nearly 100° C. This is especially the case in volcanic regions, where the earth's

temperature rises more rapidly with increase in depth below the surface than elsewhere.

Spring water is bright and sparkling, since it is more fully charged with gases than either rain or river water, and contains less organic matter, this being removed in its passage through beds of soil or gravel. The composition of some typical waters is given in the table below.

Sea Water.—The substances dissolved or suspended in river or spring water are carried to the sea and remain there, since the water vapour rising from the sea consists of practically pure water; so that, notwithstanding the removal of large quantities of these substances by settling out or by the action of organisms, sea water is very impure.

The water from the open ocean contains on the average about 3·5 per cent. of dissolved solids and has a specific gravity of about 1·03; the greater part of this soluble matter, nearly four-fifths, consists of sodium chloride, the remainder being chiefly calcium and magnesium sulphates and calcium chloride. The peculiar taste of sea water is due to the presence of these salts.

There are, however, certain land-locked seas where the evaporation is very rapid and the quantity of dissolved solids

COMPOSITION OF SOME NATURAL WATERS.

	Solids.					Gases.		
	Total Residue.	Calcium Salts	Magnesium Salts.	Sodium Chloride.	Organic Matter.	N.	O.	CO_2.
Rain Water ...	3·4	*nil.*	*nil.*	0·5	1·0	13·1	6·4	1·3
River Water (Thames)	29	20	1·8	2·6	3·4	15·0	7·4	30·3
River Water (Dee)	5·6	1·4	0·5	1·0	2·2			
Spring Water .	20			2·0	Traces	15·8	8·6	1·0
Mineral Water (Bath)	236	137	23	34	Traces	4·0	2·0	29·0
Sea Water ...	3,500	140	530	2,650	Traces	12·1	6·0	17·0

is much greater than in sea-water ; the Dead Sea, for example, contains nearly 23 per cent.

In the table (on page 168) details are given of the composition of some typical natural waters, the solids in parts per 100,000, the gases in cubic centimetres per litre.

Chemically pure water may be obtained by distillation, the water being boiled and the steam which is given off condensed. A small quantity of volatile organic matter may be carried over during a first distillation, and soluble matter from the glass condenser and receiver may be present ; but on adding a few drops of potassium permanganate solution, and distilling again in platinum apparatus, very pure water is obtained.

122. Potable Water.—When water is to be used for drinking purposes, it is of the highest importance that it should be odourless and colourless, and as free as possible from organic impurity arising from sewage contamination or contact with decaying animal or vegetable matter. It must also be free from pathogenic (disease-producing) bacteria. Dissolved salts, such as ordinarily occur in natural waters, are of less moment than organic impurity, and even such minute quantities of the latter as 0·3 or 0·4 parts per 100,000 may be injurious.

The taste of drinking water is also an important factor, and whilst distilled water and rain water are flat and insipid owing to the smaller quantity of dissolved gases which they contain, spring water has a characteristic freshness which renders it most palatable.

The water supply of towns has to be rendered pure. Filtration through large filter beds removes suspended matter. In some cases the water has also to be sterilised ; this is done by means of ozone, ultra-violet light, sodium hypochlorite, etc.

123. Industrial Water.—Each industry has its own requirements with regard to water. Thus water for laundries must be soft, water for boilers must not contain too much dissolved salts, water for dyeing and paper mills must be free from iron. Generally the water has to be chemically treated to satisfy the conditions required for the industry concerned.

124. Hardness of Water.—It is a matter of common experience that the sensation felt when washing the hands differs with waters from different sources. With rain water or the waters derived from sandstone areas a lather quickly forms, whilst with calcareous waters there is a sense of harshness and a good deal of soap is required to produce a lather; we notice further that in the latter case a scum is formed which floats on the surface of the water. Waters that readily form a lather are known as *soft* waters, whilst those which do not are called *hard* waters. Hard waters contain much dissolved matter, and especially bicarbonates and sulphates of calcium and magnesium and chlorides of sodium, magnesium, and calcium which are the chief causes of the hardness.

Soap consists of the sodium or potassium salts of certain complex acids composed of carbon, hydrogen, and oxygen (called *fatty acids*). These salts are soluble in water, and the solution possesses the remarkable property of preventing finely-divided particles of fats from running together in it. Such an intimate mixture of fat particles and water is termed an *emulsion*, and the cleansing properties of soap are due to the formation of an emulsion of any particles of grease by the action of the soapy water. Now the calcium and magnesium salts of the fatty acids present in soap are *insoluble* in water, so that on adding soap to water containing salts of these metals in solution, double decomposition immediately takes place between the soap and the salts with precipitation of the insoluble calcium and magnesium salts of the fatty acids. It is these insoluble salts which form the scum already referred to, and no soap is available for cleansing purposes till all the calcium and magnesium have been removed from the solution by precipitation.

The hardness produced by a solution of sodium chloride is due to a different cause, namely, the insolubility of soap in it.

Exp. 31. Prepare a solution of soap by dissolving a few grammes of soap in about 200 c.cm. of distilled water. Add some of this solution separately to solutions of calcium sulphate, magnesium sulphate and chloride, and sodium chloride (the last should be strong); note the flocks of insoluble calcium and magnesium salts formed in the first three cases and the curds of insoluble soap in the last.

Exp. 32. Suspend some chalk in water and pass in carbon dioxide; when the solution is saturated filter it. Shake also some chalk with water and filter. Test the two solutions by soap solution: that through which the carbon dioxide has passed is very hard; the other is soft.

The explanation of this is that chalk (calcium carbonate) is insoluble in pure water, but dissolves in water containing carbon dioxide, with formation of acid calcium carbonate or calcium bicarbonate, $Ca(HCO_3)_2$.

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

The bicarbonate reacts with soap just like any other soluble calcium salt. Magnesium bicarbonate, $Mg(HCO_3)_2$, may be formed from magnesia alba (basic magnesium carbonate) in a similar manner.

125. Temporary Hardness and its Removal. — The bicarbonates of magnesium and calcium are the chief causes of what is known as *temporary hardness*, *i.e.* hardness which can be removed by boiling.

Exp. 33. Boil some of the calcium bicarbonate solution obtained in the last experiment for a few minutes. A precipitate is formed; allow this to settle, pour off the clear liquid and add soap solution to it. No precipitate is formed, showing that the hardness has been removed.

What has happened is that on boiling, the calcium bicarbonate was decomposed into normal calcium carbonate, water and carbon dioxide.

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

The carbon dioxide passed away as a gas and the calcium carbonate was precipitated. Magnesium bicarbonate undergoes a similar decomposition on boiling.

The "fur" which forms on a steam boiler and on a kettle is chiefly calcium carbonate produced during the process of boiling.

There is another way in which temporary hardness can be removed, viz. by the addition of lime; this decomposes the bicarbonates with precipitation of normal carbonates. Cal-

cium bicarbonate, for example, is decomposed in the following manner :—

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2\,CaCO_3 + 2\,H_2O.$$

This is known as Clark's process.

126. Permanent Hardness and its Removal.—The hardness due to salts other than bicarbonates cannot be removed by boiling, and is called *permanent hardness*.

When permanent hardness is due to salts of magnesium and calcium it can be removed by the addition of washing soda ($Na_2CO_3 \cdot 10\,H_2O$), which precipitates the magnesium and calcium as insoluble carbonates—

$$\underset{\text{Calcium sulphate.}}{CaSO_4} + Na_2CO_3 = \underset{\text{ppt.}}{CaCO_3} + Na_2SO_4.$$

$$\underset{\text{Magnesium chloride.}}{MgCl_2} + Na_2CO_3 = \underset{\text{ppt.}}{MgCO_3} + 2\,NaCl.$$

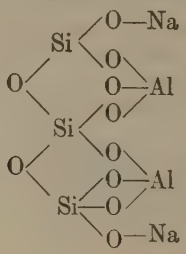
Washing soda also removes *temporary* hardness. Magnesium bicarbonate, for instance, is decomposed in the following manner :—

$$Mg(HCO_3)_2 + Na_2CO_3 = 2\,NaHCO_3 + \underset{\text{ppt}}{MgCO_3}.$$

Hardness due to sodium chloride, being caused by the insolubility of soap in the solution, cannot, of course, be removed by the addition of washing soda. There are, however, certain soaps which are soluble in brine such as *marine soap*, and these enable us to get over the difficulty.

All kinds of hardness can, of course, be removed by distillation.

The "Permutite" Process.—A method of softening water now in common use is the so-called "Permutite Process." An artificial "zeolite" is used called "permutite"; its constitution probably being as follows :—



i.e. a silicate of sodium and aluminium (hydrated). This zeolite reacts by double decomposition with calcium, magnesium, and manganese salts, and sodium is replaced by these metals. When the change is complete, the zeolite can be rendered active again by passing through it a solution of sodium chloride, from which it fixes the sodium and gives up the calcium, magnesium, etc. In practice the change is complete, and permutite removes the lime and magnesia and makes the water "soft."

127. Estimation of Hardness.—The hardness of a sample of water is determined by finding how much of a standard soap solution is required to produce a permanent lather with a known volume of the water. This gives the *total* hardness, *i.e.* the temporary and permanent hardness combined. The *permanent* hardness is found by boiling a known volume of the water for a short time to remove temporary hardness and then adding standard soap solution as before. The difference between the total and permanent hardness gives the *temporary* hardness.

Let us compare the hardnesses of various kinds of waters by performing the following experiment :—

Exp. 34. Weigh out 10 grm. of sodium oleate or green Castile soap and dissolve it in 1 litre of water. If you wish the solution to keep, it is better to use 650 c.cm. of water and 350 c.cm. of methylated spirit : this is your standard soap solution. Measure 50 c.cm. each of distilled water, rain water, well water, and sea water into 6-oz. bottles, and run the soap solution from a burette or measuring-tube into each until a lather is formed by shaking, which does not break for five minutes. Note the volume of soap solution required for each. Evaporate 20 c.cm. of each water and compare the residues in each case : the water which requires most soap for a permanent lather leaves the largest residue.

It will be found that the order of hardness is (1) sea water, (2) well water, (3) rain water and distilled water (practically equal).

128. Detection and Estimation of Water.—To distinguish water from other colourless liquids the following tests may be applied :—

(1) Add a few drops of the liquid to a small quantity of anhydrous copper sulphate (prepared by igniting some powdered blue vitriol in a crucible till it is perfectly white and allowing it to cool in a desiccator). Water rehydrates it and changes the colour from white to blue.

(2) Add a little of the liquid to some quicklime (see Exp. 30).

(3) Drop a small pellet of sodium or potassium (about the size of a pea) on to a portion of the liquid. If the liquid is water hydrogen will be evolved and will take fire in the case of potassium.

To decide whether water is *pure* or not its physical properties may be utilised. The liquid should—

(*a*) be colourless, tasteless, and odourless ;
(*b*) freeze at 0° C. ;
(*c*) boil at 100° C. under 760 mm. pressure.

Moreover, pure water should give no precipitate or coloration with (1) *silver nitrate* (showing absence of chlorides, (2) *barium chloride* (showing absence of sulphates), (3) *Nessler's solution* (showing absence of ammonia), (4) *lime water* (showing absence of carbonates).

Water is generally estimated by the loss in weight on drying, either in an oven or in a desiccator. It can be estimated gravimetrically by absorption, using a drying agent such as calcium chloride or phosphorus pentoxide.

Hydrogen Peroxide, H_2O_2.

This substance has been found in very small quantities in rain and snow, and also in the water formed by the combustion of hydrogen. It is produced in small quantity during the slow oxidation of phosphorus, and is often formed when oxidation occurs in the presence of moisture.

129. Preparation.—The peroxides of the alkali and alkaline earth metals yield hydrogen peroxide on treatment with dilute acids. Either barium peroxide or sodium peroxide is generally used in practice. The following are the details of the preparation of the pure substance using barium peroxide and sulphuric acid :—

Some dilute sulphuric acid is placed in a beaker and surrounded by a freezing mixture of ice and salt to keep its temperature low. A cream of barium peroxide and water, which has also been cooled in a freezing mixture, is then slowly run into the acid with constant stirring. Barium sulphate is precipitated and hydrogen peroxide goes into solution. Excess of barium peroxide must not be added or it will decompose the hydrogen peroxide. The best way is to add rather less than an equivalent quantity of barium peroxide (*i.e.* keep the solution acid to test paper) and remove the excess of acid by barium carbonate. The barium sulphate and any excess of barium carbonate are filtered off, and the filtrate evaporated on the water-bath, the temperature not being allowed to rise above 75° C., or the hydrogen peroxide will be decomposed. By this means a considerable part of the water is driven off.

The final purification is accomplished by fractionally distilling the liquid under reduced pressure (about 10 mm. of mercury). Water comes off first, and when this has all been removed the receiver is changed; on continuing the distillation hydrogen peroxide passes over in an almost pure state.

The equation representing the formation of hydrogen peroxide from barium peroxide and sulphuric acid is—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

130. Properties.—Hydrogen peroxide is a thick liquid with a specific gravity about 1·5; it is colourless in small masses, but in large masses it has a decidedly bluer colour than water.

Hydrogen peroxide is remarkable for the ease with which it breaks up into water and oxygen, according to the equation—

$$2\,H_2O_2 = 2\,H_2O + O_2 + 46{,}120 \text{ cal.}$$

Hydrogen peroxide is an exothermic compound, and a considerable amount of heat is set free when it decomposes, as shown above.

The pure substance is fairly stable but decomposes with explosive violence on slight rise of temperature, and the dilute aqueous solution loses oxygen rapidly on boiling.

Hydrogen peroxide affords another interesting example of catalysis, for its dilute solution decomposes rapidly at ordinary temperature in contact with certain metals such as finely-divided platinum, the latter undergoing no change. Rough surfaces hasten its decomposition. It can be rendered stable by the presence of a small amount of acetanilide.*

Commercially the strength of aqueous solutions is represented by the number of cubic centimetres of oxygen furnished by 1 c.cm. of the solution if decomposed. Thus "20 volume" hydrogen peroxide means that 1 c.cm. of the solution will yield 20 c.cm. of oxygen on decomposition.

131. Oxidising Action of Hydrogen Peroxide.—Owing to the ease with which hydrogen peroxide parts with an atom of oxygen it is a powerful oxidising agent. Thus it converts lead sulphide into lead sulphate, according to the equation—

$$PbS + 4\,H_2O_2 = PbSO_4 + 4\,H_2O.$$

Ordinary molecular oxygen will not bring about this change except on heating. We have, however, seen in discussing ozone that atomic oxygen is more active than molecular oxygen, and it is the atomic oxygen produced when hydrogen peroxide decomposes which acts so readily on the lead sulphide. We may therefore represent the reaction in two stages—

$$4\,H_2O_2 = 4\,H_2O + \underset{\text{Atomic.}}{4\,O}.$$

$$PbS + \underset{\text{Atomic.}}{4\,O} = PbSO_4.$$

This reaction is made use of in restoring the colour of old pictures which have been blackened by the action of sulphuretted hydrogen on the lead paint. The hydrogen peroxide converts the *black* lead sulphide into *white* lead sulphate. Other examples of its oxidising action are represented in the following equations :—

$$H_2S + H_2O_2 = 2\,H_2O + S.$$

$$2\,FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2\,H_2O.$$

$$2\,KI + H_2O_2 = 2\,KOH + I_2.$$

* Acetanilide, or phenylacetamide, is $C_6H_5NH.COCH_3$.

Hydrogen peroxide possesses the power of bleaching many vegetable and animal colours, and is much used for bleaching hair, silk, ivory, etc. It also destroys decaying organic matter, and consequently finds application as a disinfectant. Both these properties depend upon its oxidising action.

Hydrogen peroxide forms peroxides with alkalies

$$2\,NaOH + H_2O_2 \rightleftharpoons Na_2O_2 + 2\,H_2O$$
$$CaO + H_2O_2 = CaO_2 + H_2O$$
$$Ba(OH)_2 + H_2O_2 = BaO_2 + 2\,H_2O.$$

In these cases hydrogen peroxide behaves as an acid, and it is interesting to note in confirmation that if sodium carbonate is added to hydrogen peroxide, sodium peroxide is formed and carbon dioxide is evolved.

$$Na_2CO_3 + H_2O_2 = Na_2O_2 + CO_2 + H_2O.$$

Hydrogen peroxide gives an orange yellow coloration with titanium salts, the depth of colour depending on the amount of titanium present, and it is therefore used for the estimation of titanium.

132. Reducing Action of Hydrogen Peroxide.—When silver oxide, Ag_2O, is treated with hydrogen peroxide a mutual decomposition takes place; the silver oxide is reduced to silver and the hydrogen peroxide to water, and a molecule of oxygen is evolved—

$$Ag_2O + H_2O_2 = 2\,Ag + H_2O + O_2.$$

A probable explanation of this is that both silver oxide and hydrogen peroxide contain a loosely-combined atom of oxygen, and the attraction of these two atoms for one another is greater than their respective attractions for silver and water. They consequently break away and unite to form a molecule of oxygen. We may represent this in the following way, a thick arrow indicating greater attracting force than a thin arrow—

$$Ag_2 \leftarrow O \rightarrow\!\leftarrow O \rightarrow OH_2.$$

Other examples of the reducing action of hydrogen peroxide explained in a similar manner are represented by the following equations :—

$$2\ CrO_3 + 3\ H_2O_2 = Cr_2O_3 + 3\ H_2O + 3\ O_2.$$

$$H_2O_2 + O_3 = H_2O + 2\ O_2.$$

Potassium permanganate in acid solution is also reduced—

$$2\ KMnO_4 + 4\ H_2SO_4 + 5\ H_2O_2 = 2\ KHSO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ O_2.$$

133. Experiments with Hydrogen Peroxide.—To illustrate the properties of hydrogen peroxide, the following experiments may be performed :—

Exp. 35. (1) To some dilute hydrogen peroxide add potassium iodide, iodine will be liberated, and the solution become brown. The equation for the reaction which takes place has been given in § 131.

(2) Make a dark stain of sulphide of lead on filter paper by first moistening it with a solution of a lead salt, say the acetate, and then exposing this to sulphuretted hydrogen. Steep the paper in a little of the hydrogen peroxide solution and it will become white, the black sulphide of lead having been transformed into the white sulphate, as shown in the equation given above.

(3) Add silver nitrate to some of the solution, and then caustic soda ; a black precipitate of hydrated oxide of silver will be formed, and this in contact with the hydrogen peroxide will undergo decomposition in the manner already described ; the effervescence of gas which is seen to occur may be shown to be due to oxygen.

(4) Acidify a few c.cm. of the solution, add a little ether, then a few drops of a solution of potassium dichromate, and shake. A blue colour is imparted to the ether, probably due to perchromic acid.

(5) Mix 1 c.cm. of ferric chloride with 1 c.cm. of potassium ferricyanide. Add one drop of hydrogen peroxide : Prussian Blue is formed.

Nos. 4 and 5 are " delicate " tests.

134. Distinction between Hydrogen Peroxide and Ozone.—We have seen that both ozone and hydrogen peroxide liberate iodine from potassium iodide. In the presence of *ferrous sulphate*, however, hydrogen peroxide is the *only oxidising agent* which can do this, and we are thus able to distinguish hydrogen peroxide from all other oxidising agents, including, of course, ozone.

135. Proof of the Composition of Hydrogen Peroxide.—The following method may be adopted to prove that the ratio of oxygen to hydrogen in hydrogen peroxide is twice as great as it is in water :—A given weight (about 0·2 grm.) of the pure substance, prepared as already described, is introduced into a flask, which is then filled up completely with recently-boiled water. This flask is provided with a delivery tube which does not reach below the bottom of the cork, and is also filled with water. The flask is heated at first to about 80° C., but finally (when the evolution of gas slackens) to the boiling-point. Oxygen is evolved, and is collected over water in a measuring tube of about 100 c.cm. capacity.

The weight of oxygen evolved can be calculated from its volume, and if the hydrogen peroxide is pure it will be found that 34 parts by weight of it yield 16 parts by weight of oxygen. The remaining $34 - 16 = 18$ parts by weight consist of water. Now 18 parts by weight of water contain 16 parts by weight of oxygen and 2 parts by weight of hydrogen. Therefore the ratio of oxygen to hydrogen in hydrogen peroxide is $2 \times 16 : 2 = 16 : 1$, which is twice as great as the ratio in water (approximately 8 : 1).

The simplest formula for hydrogen peroxide would be HO, for 1 and 16 are the atomic weights of hydrogen and oxygen. It has been proved, however, by a physical method of determining molecular weights (the lowering of freezing-point method), that the molecular weight is not 17 as it would be if the formula were HO, but 34, which corresponds to the formula H_2O_2. The doubled formula possesses the advantage that it fits in with the usual valencies of hydrogen (one) and oxygen (two). Thus the structural formula would be—

$$H - O - O - H.$$

If, however, the single formula were adopted, both oxygen and hydrogen must have the same valency, the structural formula being H — O.

136. Detection and Estimation.—Hydrogen peroxide can readily be detected by the tests mentioned above. It is estimated by determining the iodine liberated from potassium

iodide, or by the reduction of potassium permanganate by direct titration.

QUESTIONS.—CHAPTER XIII.

1. Describe carefully a synthetic method of determining the composition of water by volume.

2. How may the volumetric composition of water be determined analytically ?

3. How would you prove by experiment that steam contains its own volume of hydrogen ?

4. Describe the method by which Dumas and Stas determined the composition of water by weight.

5. Pure hydrogen is passed over heated oxide of copper, and the water which forms is collected ; if the loss in weight of the oxide of copper be 4·20 grm., and the weight of the water obtained 4·73 grm., determine the amount of hydrogen and oxygen in 100 grm. of water.

6. How can permanent hardness be removed from water ?

7. How can the temporary and permanent hardness in a sample of water be determined ?

8. What is meant by *water of crystallisation ?* Give examples.

9. Distinguish between a *hydrate* and a *hydroxide*, and give examples of each.

10. Write down in separate paragraphs (*a*) the physical, (*b*) the chemical properties of water.

11. Make a list of those properties of water which you regard as being absolutely characteristic of that body.

12. How would you test whether a given colourless liquid is water or not ?

13. How is hydrogen peroxide prepared ? What is its action on (1) potassium iodide, (2) lead sulphide, (3) silver oxide ?

14. It has been said that hydrogen peroxide behaves both as an oxidising and a reducing agent ; explain this statement, and illustrate your remarks by references to reactions.

15. How can the composition of hydrogen peroxide be determined ?

16. Describe a test by which hydrogen peroxide and ozone can be distinguished.

CHAPTER XIV.

THE HALOGENS.

A comparison of the physical and chemical properties of the four elements, fluorine, chlorine, bromine, and iodine, and of their compounds, readily leads one to regard these elements as forming a natural group.

This is shown in two ways, firstly by the *resemblance* in properties, and secondly by the *gradual transition* in their properties, which proceeds always in the same order, viz. in the order of their atomic weights. A general survey of the group will illustrate this.

137. Physical Properties of these Elements.—Fluorine is a gas which condenses to a liquid when cooled to a temperature of — 187° C. ; it possesses a very faint greenish-yellow colour ; chlorine is a much more readily-condensible gas, and has a distinct greenish colour ; bromine is a dark red liquid boiling at 58·6° C. and solidifying at — 7° C. ; whilst iodine is a black crystalline solid which boils at 183° C., its vapour being of a beautiful violet colour.

In the gaseous condition these elements have a very irritant action on the mucous membrane, which is, however, much less marked in the case of iodine than in that of the other three elements. The halogens have an odour resembling that of sea-weed if they are in a largely-diluted condition.

Their solubility in water follows the order of their atomic weight as far as chlorine and iodine are concerned, but bromine is an exception, whilst fluorine decomposes water. Thus chlorine dissolves in about half its volume of water, whilst iodine is only very slightly soluble. Bromine, however,

dissolves to the extent of 3 parts in 100 by weight, which corresponds to about 4 volumes of bromine as vapour in 1 volume of water.

When chlorine is passed into water to saturation at 0° C., yellow crystals having the composition $Cl_2 \cdot 8\,H_2O$ separate out. On warming these crystals they readily decompose with the evolution of chlorine. Bromine under similar circumstances forms crystals having the composition $Br_2 \cdot 10\,H_2O$.

138. General Chemical Properties.—All the halogens combine directly with hydrogen to form gases (except hydrofluoric acid, which is a liquid boiling at 19·5° C.). These hydrides of the halogens are very soluble in water, giving rise to strongly acid solutions. The readiness with which combination with hydrogen takes place *decreases* as the atomic weight *increases*. Thus, fluorine and hydrogen combine even in the dark and at very low temperatures, whereas chlorine requires the influence of heat or of chemically active light rays, and bromine and iodine are induced to combine with hydrogen with much greater difficulty.

Moreover, the stability of the products, HF, HCl, HBr, HI, shows a falling off in the order named.

The hydrogen atom of each of these compounds can be replaced by the metals potassium and sodium to form a group of bodies, KF, NaF, KCl, etc., all of which closely resemble *sea-salt*. It is from this that the name *halogens* is derived (Greek, *hals*, sea salt, and *gennao*, I produce).

The tendency of the halogens to combine with oxygen *increases* as the atomic weight *increases*. (Thus, whilst fluorine forms no oxide) and chlorine can only be made to combine with oxygen indirectly giving rise to unstable oxides, iodine is directly oxidised by nitric acid, and its oxide is much more stable. (Bromine occupies an anomalous position here, as no oxide of it is known)

The interaction of the halogens and water affords another example of this gradation in properties as we pass from fluorine to iodine. Fluorine decomposes water immediately at ordinary temperatures, a vigorous reaction taking place; much of the oxygen liberated is in the form of ozone. Chlorine

and bromine act on water at ordinary temperatures only in the presence of sunlight, and no ozone is formed; chlorine is much the more active of the two. Iodine does not decompose water.

Chlorine and iodine, and bromine and iodine, unite with one another to form unstable compounds.

Fluorine, F_2.

139. History.—The existence of fluorine was first proved by Davy in the year 1813. He showed that hydrofluoric acid was similar in composition to hydrochloric acid, *i.e.* it consisted of hydrogen, combined with an element resembling chlorine, which was unknown in the free state, and which he called Fluorine, because he said: "Fluorspar and analogous substances must be regarded as binary compounds of metals and fluorine." Davy tried to isolate the element from an aqueous solution of hydrofluoric acid, in the same way that chlorine can be obtained from an aqueous solution of hydrochloric acid, *i.e.* by electrolysis. The products were, however, found to consist not of hydrogen and a new element, but of hydrogen and oxygen.

Davy then experimented with stronger solutions of the acid, but he found that the stronger the solution the weaker was its conducting power, and the anhydrous acid did not conduct at all. Gay-Lussac and Thénard also tried the electrolytic method without success. Then Davy tried to decompose a number of fluorides by the action of chlorine. His experiments were again unsuccessful; if the unknown element was formed at all it immediately attacked the containing vessel.

The connecting link between Davy's electrolytic experiments and the isolation of fluorine by Moissan, in 1886, was provided by Gore, who showed that anhydrous hydrofluoric acid is rendered conducting by dissolving hydrogen potassium fluoride in it. By electrolysing such a solution in a platinum U-tube Moissan obtained free fluorine.

140. Occurrence.—The chief naturally occurring compound of fluorine is *fluorspar*, calcium fluoride, CaF_2. This is found in large quantities amongst the limestone rocks of Derbyshire.

Other minerals containing fluorine are *cryolite*, Na_3AlF_6, and *apatite*, $3\,Ca(PO_4)_2 + CaF_2$. It is also found in many river waters, in the blood, bones, teeth, and brains of animals.

141. Preparation.—The apparatus which Moissan used (Fig. 28) consisted of a U-tube made of platinum, which was cooled to $-23°$ by the evaporation of liquid methyl chloride. The tube was provided with side tubes for leading away the products of electrolysis, and the electrodes E, made of an alloy of platinum and iridium, were insulated

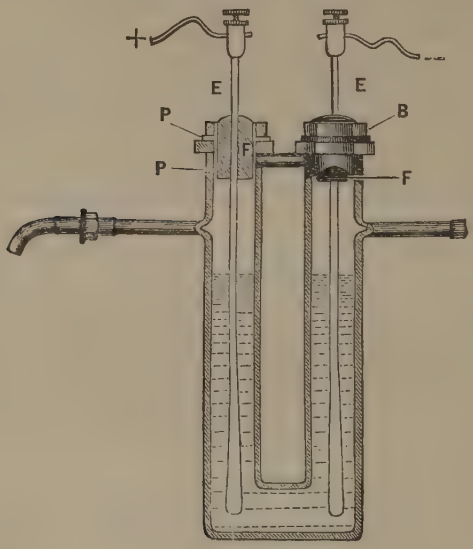


Fig. 28.

from the U-tube by means of fluorspar stoppers, F. The joints were made gas-tight by means of lead washers, P, screwed down by the brass caps B. The electrodes were thickened at the lower end, as they are gradually eaten away by the fluorine. The U-tube was about two-thirds filled with

a solution of one part of hydrogen potassium fluoride in five parts of anhydrous hydrofluoric acid.

On passing a current from about 25 Bunsen cells, hydrogen was evolved at the negative electrode and fluorine at the positive electrode. The fluorine was led through a platinum spiral immersed in boiling methyl chloride, in which most of the hydrofluoric acid condensed and was finally purified by passing over sodium fluoride contained in a platinum tube. This combined with any remaining hydrofluoric acid, with formation of hydrogen sodium fluoride, $NaHF_2$—

$$NaF + HF = NaHF_2.$$

The gas was collected in a platinum vessel by displacement of air.

Moissan also prepared the gas by direct electrolysis of fused potassium hydrogen fluoride, and he replaced the platinum with a copper vessel, but the electrodes were made of an alloy of platinum and iridium, as before. This is now the general method for the preparation of fluorine.

142. Properties.—Fluorine is a greenish-yellow gas which has a very irritant action on the mucous membrane. It is somewhat heavier than air, possessing a vapour density 19 (H = 1). This corresponds to a molecular weight 38, and since the atomic weight of fluorine is 19 its molecule contains two atoms (F_2). Fluorine is the most chemically active substance known, and attacks most substances with violence even at ordinary temperatures. All the elements combine with it except oxygen, and the members of the helium group. Hydrogen and fluorine explode when mixed, even in the dark. The metals sodium, potassium, magnesium, mercury, and many others are violently attacked, but copper, gold, and platinum are more resistant. Sulphur, phosphorus, silicon, boron, carbon, iodine, and arsenic all combine with fluorine at ordinary temperatures with production of flame.

As already stated, fluorine decomposes water at ordinary temperature with liberation of a mixture of oxygen and ozone—

$$2\,F_2 + 2\,H_2O = O_2 + 4\,HF.$$
$$3\,F_2 + 3\,H_2O = O_3 + 6\,HF.$$

It immediately breaks up compounds of the other halogens, such as hydrochloric acid and potassium bromide, with liberation of the free halogen and formation of the corresponding fluoride—

$$2\,HCl + F_2 = 2\,HF + Cl_2.$$
$$2\,KBr + F_2 = 2\,KF + Br_2.$$

Sulphur dioxide, sulphuretted hydrogen, ammonia and even silica (and consequently glass) are all rapidly decomposed. Dry fluorine has little or no action on glass, but if a trace of moisture is present it readily attacks the glass forming silicon tetrafluoride, SiF_4. Here we have another case of water acting as a catalyst.

Fluorine violently attacks organic substances, many of which (*e.g.* alcohol) take fire.

Liquid and Solid Fluorine.—At — 187° C. fluorine condenses to a yellow mobile liquid, which is not much less active than the gas, *e.g.* it combines with liquid hydrogen with explosive violence. It does not, however, unite with iodine.

Fluorine can be obtained as a pale yellow solid melting at a temperature of — 233° C.

Chlorine, Cl_2.

143. History.—This element was discovered by Scheele in 1774, in a research on the black oxide of manganese—a research which also led to the discovery of oxygen in the same year. Scheele obtained chlorine in the way in which it is still usually prepared. He called it "dephlogisticated marine acid gas," considering it, in accordance with the ideas of the time, as a compound of hydrochloric acid ("marine acid gas") with oxygen. Chlorine was thus considered to be a compound of oxygen and muriatic acid till 1789, when Lavoisier called it *oxymuriatic acid*, because on exposure of an aqueous solution of "dephlogisticated marine acid gas" to light, bubbles of oxygen were evolved, and the solution remaining was muriatic acid.

Davy suggested that if it were a compound it could be decomposed into its elements. From the results of many

experiments, notably the heating of metallic sodium in oxymuriatic acid when *only* sodium muriate was obtained, Davy (1810) said it was an element, and suggested that the name oxymuriatic acid was not fitting and therefore called it chlorine (Greek, *chloros*, greenish-yellow).

Davy also proved that hydrochloric acid does not contain any oxygen, and that hydrochloric acid is a compound of hydrogen and chlorine only.* This was an important matter, because Lavoisier's experiments had given rise to the idea that all acids contain oxygen. Davy's proof of the constitution of hydrochloric acid gave the death-blow to this oxygen-theory of acids, and prepared the way for the hydrogen-theory that was to follow it.

144. Occurrence.—Chlorine occurs very abundantly in nature, but never in the free state. Its most important compound is common salt (sodium chloride), which forms large deposits in various parts of the world, *e.g.* Cheshire in England, and Wieliczka in Galicia. Common salt is also the chief solid constituent of sea water. The enormous salt deposits at Stassfurt in Germany are composed largely of the chlorides of potassium and magnesium. Free hydrochloric acid is a constituent of the gastric juice.

145. Preparation.—Chlorine is usually prepared in the laboratory by heating manganese dioxide with concentrated hydrochloric acid. The reaction which takes place is represented by the equation—

$$\underset{\text{Manganese dioxide.}}{MnO_2} + 4\,HCl = \underset{\text{Manganous chloride.}}{MnCl_2} + 2\,H_2O + Cl_2.$$

Exp. 36. Introduce about 100 grm. of manganese dioxide, in small lumps, into a large flask, and just cover it with strong hydrochloric acid. Close the mouth of the flask with an indiarubber cork carrying a safety funnel and delivery tube. Support the flask on a sand-bath by means of a retort-stand, and connect it with a wash-bottle containing

* Gay-Lussac and Thénard had previously suggested that chlorine might be an element, although they said it could equally be considered a compound.

a little water. Provide the wash-bottle with a delivery tube reaching to the bottom of a glass cylinder as shown in Fig. 29. Now apply a gentle heat to the flask, when chlorine is evolved mixed with hydrochloric acid.

For a short time, both the chlorine and the hydrochloric are absorbed by the water in the wash-bottle. Soon, however, the solution becomes saturated with chlorine which then passes on, whilst the hydrochloric acid, being very much more soluble, continues to be absorbed in the wash-bottle. The chlorine is collected in glass cylinders by displacement of air; it cannot be collected over water or mercury because it is soluble in the former and attacks the latter; it may, however, be collected over strong brine in which it is only slightly soluble.

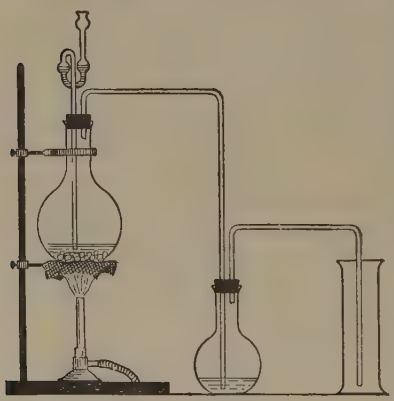


Fig. 29.

If the gas is required *dry* it may be passed through one or more wash-bottles containing concentrated sulphuric acid before being collected as above.

Instead of using hydrochloric acid in the preparation of chlorine just described, a mixture of common salt and strong sulphuric acid may be employed. The equation representing the reaction which takes place then becomes—

$$MnO_2 + 3\,H_2SO_4 + 2\,NaCl = MnSO_4 + 2\,NaHSO_4 + 2\,H_2O + Cl_2.$$

Another convenient method of preparing chlorine is to act on bleaching powder with dilute hydrochloric acid. The bleaching powder is used in the form of small lumps, obtained by first pressing it into a cake and then breaking up this cake. Under these conditions chlorine is evolved at a convenient rate without the application of heat—

$$\underset{\text{Bleaching powder.}}{CaOCl_2} + 2\,HCl = \underset{\text{Calcium chloride.}}{CaCl_2} + H_2O + Cl_2.$$

Fairly pure chlorine can be obtained by heating potassium dichromate with hydrochloric acid—

$$K_2Cr_2O_7 + 14\ HCl = 2\ KCl + Cr_2Cl_6 + 3\ Cl_2 + 7\ H_2O.$$

Also by allowing hydrochloric acid to drop on potassium permanganate in the cold, chlorine is evolved—

$$2\ KMnO_4 + 16\ HCl = 2\ KCl + 2\ MnCl_2 + 5\ Cl_2 + 8\ H_2O.$$

Chemically pure chlorine can be prepared by decomposing potassium platinichloride at a red heat—

$$K_2PtCl_6 = 2\ KCl + Pt + 2\ Cl_2$$

or by the electrolysis of pure fused silver chloride.

146. Electrolytic Process.—Chlorine is now prepared industrially by the electrolysis of sodium chloride; generally brine. It is largely a by-product in the manufacture of electrolytic caustic soda. This method of manufacture was delayed owing to the many technical difficulties encountered. Thus chlorine being very active chemically, attacked the metallic parts of the plant, and it was only when methods of keeping apart the products of the reaction were successful that the electrolytic process was generally adopted.

In the case of brine—

$$NaCl = Na^{\cdot} + Cl'.$$

Sodium is liberated at the cathode and reacts with the water to form sodium hydroxide and hydrogen. Chlorine is liberated at the anode, which is made of graphite or magnetic oxide of iron, both of which are unaffected by the gas. Details of the apparatus, etc., are given under Caustic Soda in *Inorganic Chemistry, Mainly Metals.*

147. Weldon Process.—Chlorine was formerly prepared on the large scale from the same materials (MnO_2 and HCl) as are employed in the laboratory. The charge of manganese dioxide and hydrochloric acid was heated by high pressure steam.

The residue in the still at the end of the operation was acid, and contained the manganese in solution as chloride

($MnCl_2$); this originally was run off to waste, but by the *Weldon recovery process* it was possible to get most of the manganese back in the form of peroxide.

The essential part of this process consisted in blowing air through the hot liquor in the presence of lime. Manganese peroxide was formed and combined with the lime to form calcium manganite ($CaO.\ 2\ MnO_2$ or $CaMn_2O_5$), which was known as "manganese mud." It was found that the presence of a base was necessary; it induced the formation of an acidic oxide (manganese dioxide is an acidic oxide in manganites) with which it can combine to form a salt.

The product so obtained had about 80 per cent. of the value for evolving chlorine of the original ore used, and when as much clear liquid as possible had been run off from it (after settling), this mud was run into the still and used over again. In so finely divided a condition the action would have been too violent, and in order to check the rapidity of evolution of the chlorine it was usual to charge the requisite amount of hydrochloric acid into the still first and then run in the manganese mud gradually.

In addition to the process just described chlorine was manufactured by two other processes, namely the "Deacon" process and the "Péchiney-Weldon" process.

148. The "Deacon" Process.—This process depends upon the fact that on heating hydrochloric acid gas and oxygen together at high temperature a partial decomposition takes place, with formation of chlorine and steam—

$$4\ HCl + O_2 = 2\ H_2O + 2\ Cl_2.$$

The decomposition is greatly assisted by the presence of certain substances (*e.g.* cupric chloride) which act as catalytic agents.

The process is carried out as follows:—A mixture of hydrochloric acid gas and air in the proportion of four to one by volume is heated up to 500° C., and passed over broken bricks which have been caused to take up cupric chloride by dipping in a solution of the salt. The resulting chlorine is mixed with large quantities of hydrochloric acid gas, water

vapour, nitrogen, and oxygen; of these the hydrochloric acid gas and the water vapour must be removed before the chlorine can be used in the manufacture of bleaching powder—the chief purpose for which it is employed. The mixed gases are cooled and then passed up a tower filled with flints down which Weldon's mud trickles; this converts the hydrochloric acid into chlorine. The water vapour is then removed by passing through sulphuric acid.

It is supposed that the cupric chloride undergoes the following cycle of operations:—At the high temperature to which it is subjected it is broken up into cuprous chloride, Cu_2Cl_2, and chlorine—

$$2\ CuCl_2 = Cu_2Cl_2 + Cl_2.$$

The oxygen present then combines with the cuprous chloride forming an oxychloride—

$$2\ Cu_2Cl_2 + O_2 = 2\ Cu_2OCl_2.$$

This oxychloride is, however, at once decomposed by hydrochloric acid with reformation of cupric chloride—

$$Cu_2OCl_2 + 2\ HCl = 2\ CuCl_2 + H_2O.$$

The whole cycle of operations is then repeated. Since the cupric chloride transfers oxygen from the air to the hydrogen of the acid it is called an *oxygen carrier*.

149. The Péchiney-Weldon Process.—When the oxychloride of magnesium obtained by adding magnesia (MgO) to a solution of magnesium chloride ($MgCl_2$) is heated strongly, it decomposes with formation of hydrochloric acid* and chlorine,† and a residue of magnesia remains. This change forms the basis of the Péchiney-Weldon process which is used to some extent for the manufacture of chlorine. The hydrochloric acid mixed with the chlorine is converted into chlorine by means of Weldon's mud as described under the last process; or else it is removed by passing through water. The residue of magnesia can be used over again.

* The hydrogen of the hydrochloric acid is derived from the water present in the oxychloride.

† Oxygen of the air replaces the chlorine of the $MgCl_2$.

This method can only be used economically and conveniently at places where magnesium chloride is very cheap.

150. Properties.—Chlorine is a greenish-yellow gas which has a very irritant action on the mucous membrane. It is soluble in water, one volume of which takes up about two volumes of the gas at ordinary temperatures. Chlorine is a heavy gas, its density being about two and a half times that of air. Its molecule contains two atoms, except at very high temperatures, when partial dissociation into single atoms takes place, as shown by the fall in vapour density.

Chlorine is a very active substance. Thus it displaces iodine from iodides and bromine from bromides—

$$2\,KI + Cl_2 = 2\,KCl + I_2$$

$$2\,KBr + Cl_2 = 2\,KCl + Br_2$$

It combines directly with many elements and compounds at the ordinary temperature, very frequently with incandescence. Chlorine is sent out into commerce in the liquid state stored in iron cylinders.

151. Combination of Chlorine and Hydrogen.—When chlorine and hydrogen are mixed and exposed to direct sunlight they combine with explosion, hydrochloric acid being formed. Burning magnesium wire, which gives out light very rich in chemically active rays, also causes the mixture to explode. In diffused daylight combination takes place gradually, and in the dark hydrogen and chlorine do not unite. By proceeding as described in the following experiment it is possible to burn hydrogen quietly in chlorine.

Exp. 37. Prepare a jar of chlorine from manganese dioxide and hydrochloric acid as described above, and introduce a lighted jet of hydrogen into it. It continues to burn with the production of fumes of hydrochloric acid, which may be made more visible by bringing a drop of ammonia liquor to the mouth of the jar.

The affinity of chlorine for hydrogen is so great that it is able to extract it from many compounds, such as turpentine ($C_{10}H_{16}$), sulphuretted hydrogen and water.

Exp. 38. Introduce a piece of blotting-paper soaked in turpentine into a jar of chlorine. The turpentine takes fire; white fumes of hydrochloric acid are formed and a black deposit of free carbon settles on the sides of the jar.

$$C_{10}H_{16} + 8\,Cl_2 = 10\,C + 16\,HCl.$$

Exp. 39. Pass chlorine for some minutes through about 50 c.cm. of water, and to about 20 c.cm. of this add a solution of sulphuretted hydrogen; hydrochloric acid is formed, the liquid becoming turbid owing to the separation of sulphur, according to the equation—

$$Cl_2 + H_2S = 2\,HCl + S.$$

Exp. 40. Fill a glass tube of wide bore, about 10 in. long, fitted with a cork at one end, with chlorine water. Place the open end in a trough of water and expose to direct sunlight; bubbles of gas will be seen to rise in the liquid. When sufficient gas has collected it may be tested with a glowing splinter, and will be found to be oxygen.

The change which has taken place is represented by the equation—

$$8\,Cl_2 + 8\,H_2O = 14\,HCl + 2\,HClO_3 + O_2.$$

Chlorine will, moreover, support the combustion of a candle or of coal gas, on account of its affinity for hydrogen. The substances of which candles are composed consist either entirely, or at any rate largely, of carbon and hydrogen, and when a lighted candle is lowered into a jar of chlorine it continues to burn with formation of hydrochloric acid and separation of carbon, just as in the case of turpentine.

Exp. 41. Fix a piece of candle into a deflagrating spoon, light it, and lower into a jar of chlorine. The candle continues to burn with a dull red smoky flame and soot is deposited on the walls of the jar.

Coal gas, again, consists almost entirely of a mixture of free hydrogen and compounds of carbon and hydrogen, and when a jet of lighted coal gas is lowered into a jar of chlorine it continues to burn, but the flame becomes duller and smoky owing to the separation of free carbon.

152. Combination of other Elements with Chlorine.—

Exp. 42. Into a jar of chlorine bring a piece of phosphorus on a deflagrating spoon and without the application of heat; presently the

phosphorus will ignite and burn feebly with the formation of phosphorus trichloride—

$$P_4 + 6\,Cl_2 = 4\,PCl_3.$$

Antimony, copper, and some other metals in a finely-divided condition, also ignite when plunged into chlorine.

Exp. 43. Heat a piece of sodium in a deflagrating spoon until it takes fire, and then plunge it into a jar of chlorine; the sodium burns brilliantly, uniting with the chlorine to form sodium chloride.

153. Inactivity of Dry Chlorine.—It is found that, though as we have seen, moist chlorine is a very active substance, *perfectly dry* chlorine is comparatively inactive. Thus, sodium even when heated does not combine with dry chlorine. Here, then, we meet with another example of the phenomenon already encountered in the case of hydrogen and oxygen, that the presence of water is necessary in order that a chemical reaction may take place.

154. Action of Chlorine on the Alkalies.—If chlorine is passed into a *cold* solution of sodium hydroxide, sodium hypochlorite, sodium chloride, and water are formed—

$$Cl_2 + 2\,NaOH = NaOCl + NaCl + H_2O.$$

If a *hot* solution of caustic soda is used sodium chlorate and sodium chloride are formed—

$$3\,Cl_2 + 6\,NaOH = 5\,NaCl + NaClO_3 + 3\,H_2O.$$

155. Oxidising Action of Chlorine.—Chlorine is a strong oxidising agent *in the presence of moisture*, this property depending on its power of combining with the hydrogen of water and liberating *nascent* oxygen—

$$Cl_2 + H_2O = 2\,HCl + O.$$

An example of such action is its power of converting sulphurous acid into sulphuric acid.

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + H_2O + Cl_2 = \underset{\text{Sulphuric acid.}}{H_2SO_4} + 2\,HCl.$$

Another example is furnished by the *bleaching** properties of chlorine; vegetable colouring matters, *e.g.* the pigments in the leaves and flowers of plants are deprived of their colour by moist chlorine, though in the absence of moisture no such action takes place.

Exp. 44. Prepare a jar of dry chlorine (using two sulphuric acid wash-bottles). Place in this a piece of cloth dyed with turkey-red and leave it some minutes with the cover on; no decolorisation will occur, but on moistening the cloth it will be bleached.

Chlorine converts lower chlorides into the higher chloride, *e.g.*—

$$2\ FeCl_2 + Cl_2 = 2\ FeCl_3$$
$$SnCl_2 + Cl_2 = SnCl_4$$

and is in these cases an "oxidising agent."

156. Action of Chlorine on Organic Substances.—Many organic substances are very readily attacked by chlorine. In some cases (*e.g.* ethylene) the chlorine simply adds itself on to the compound, and *addition products* are formed.

$$C_2H_4 + Cl_2 = \underset{\text{Ethylene dichloride.}}{C_2H_4Cl_2}.$$

In other cases (*e.g.* marsh gas), chlorine replaces one or more atoms of hydrogen, and *substitution products* result—

$$CH_4 + Cl_2 = \underset{\text{Methyl chloride.}}{CH_3Cl} + Cl_2.$$

The displaced hydrogen combines with more chlorine forming hydrochloric acid. We shall return to this subject when studying the hydrocarbons.

Chlorine is a very powerful *disinfectant*, as it rapidly kills the minute forms of life known as bacteria, which are the chief cause of the putrefaction of organic matter. Chlorine combines with carbon monoxide and with sulphur dioxide in

* Chlorine water also yields hypochlorous acid, which is a strong bleaching agent—

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

sunlight, or when a catalyst is present to form carbonyl chloride and sulphuryl chloride respectively—

$$CO + Cl_2 = COCl_2$$

$$SO_2 + Cl_2 = SO_2Cl_2.$$

157. Chlorine Water.—Chlorine dissolves in water (4·6 c.cm. of chlorine in 1 c.cm. of water at 0° C.) to form chlorine water. On cooling a saturated solution of chlorine in water crystals of *chlorine hydrate*, $Cl_2.8\ H_2O$, are obtained, but these decompose on rise of temperature, giving chlorine. Chlorine water is an oxidising agent (see § 155).

158. Liquid and Solid Chlorine.—Chlorine can readily be liquefied. Liquid chlorine is an orange-yellow substance of specific gravity 1·56; it boils at — 34° C. and freezes at — 102° C.

Liquid chlorine is used extensively for bleaching, for the preparation of various chlorine compounds, notably carbon tetrachloride, in the manufacture of bromine and in extracting gold.

Bromine, Br_2.

159. History.—Bromine was discovered by Balard in 1826. He obtained it by distilling the mother liquors from the production of sea salt after passing in chlorine. Balard, like Liebig, thought it was iodine chloride, but after failing to detect any iodine in his product, he said it was an element and called it bromine (Greek, *bromos*, a stench).

160. Occurrence.—Bromine does not occur in the free state in nature. It is found in small quantities in combination with certain metals, chiefly potassium, sodium, magnesium, and calcium, in sea water and in many mineral waters. The salt deposits of Stassfurt contain a small percentage of bromides, and it is from this source that most of the bromine of commerce is obtained.

161. Preparation.—Bromine may be prepared from sodium bromide or potassium bromide by heating with strong sulphuric acid and manganese dioxide, just as chlorine is prepared from common salt.

$$2\,KBr + 3\,H_2SO_4 + MnO_2 = 2\,KHSO_4 + MnSO_4 + 2\,H_2O + Br_2.$$

Exp. 45. Introduce into a tubulated retort a mixture of about 20 grm. of potassium bromide and 10 grm. of manganese dioxide. Cover the mixture with strong sulphuric acid poured in through a funnel inserted in the tubulus of the retort. Insert the stopper and place over the open end of the retort a flask resting in a trough of water and covered over with a wet cloth, as shown in the diagram (Fig. 30). On gently heating the mixture bromine distils over and condenses in the cooled receiver, where it collects as a dark-red liquid. Since the vapours of bromine are very injurious, the operation *must* be performed in a fume cupboard with a *good draught.*

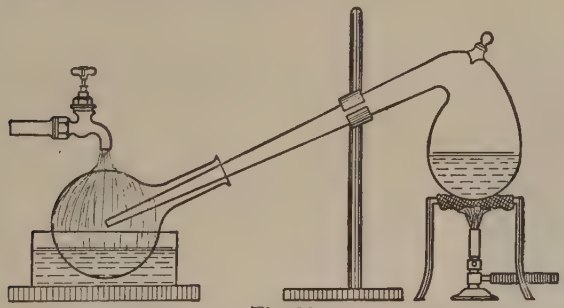


Fig. 30.

162. Manufacture.—On the large scale bromine is obtained from the liquors which remain after the extraction of potassium chloride from carnallite ($KCl + MgCl_2 + 6\,H_2O$) as carried out at Stassfurt. These liquors contain about 0·25 per cent. of bromine, which is present as magnesium bromide. Now when a bromide is treated with chlorine the latter displaces the bromine and forms the corresponding chloride. In the case of magnesium bromide the equation representing the reaction is—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

It is this reaction which is made use of in the manufacture of bromine. A diagrammatic sketch of the plant is given in

Fig. 31. The hot mother liquor is introduced through a tube, B, into a tower, A, filled with earthenware balls. By an arrangement not shown in the diagram, it is spread uniformly over the surface of these and flows slowly down the tower. On reaching the bottom it is conveyed by a pipe D to a tank W, which is provided with a number of ledges as shown in the diagram; the liquor circulates round these, as indicated by the arrows. It finally flows out of the tank by the waste pipe C, the open end of which is slightly below the level of the top of the tank; this ensures that the latter is always nearly full of liquid.

A stream of chlorine enters the tank by the pipe K and passes along the tube D and up the tower A, where it meets the descending mother liquor. Bromine is liberated in accordance with the equation given above, and passes away as vapour by the tube L. Any bromine which dissolves in the liquid in the tower is driven out of solution on reaching the tank by a current of steam introduced by the pipe E, and is carried up into the tower again by the stream of chlorine. The bromine vapour is led through a worm immersed in cold water, where it condenses to the liquid state and runs into a stone jar. Any uncondensed bromine which escapes from this is absorbed in a tower filled with moist iron filings, which convert it into ferrous bromide ($FeBr_2$).

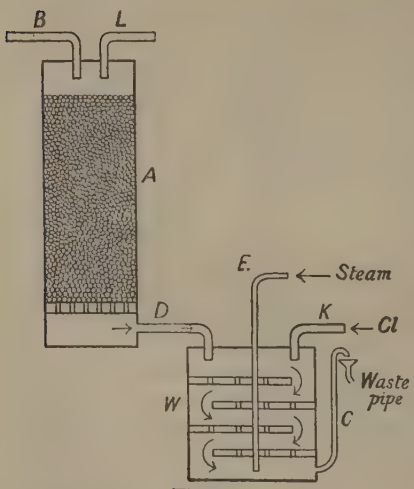


Fig. 31.

The bromine obtained in this way is impure; it is said to contain bromine chloride, BrCl, and often bromine iodide,

BrI. It is purified by agitating with potassium bromide solution and zinc oxide, and re-distilling. The chlorine remains behind as potassium chloride and the iodine is retained by the zinc oxide.

163. Properties.—Bromine is a heavy, mobile, dark-red liquid, possessing a very offensive odour. Its action on the mucous membrane is worse even than that of chlorine. Bromine has a specific gravity of 3·188 (water = 1) at 0° C., it boils at 58·6° C., the vapour possessing the same colour as the liquid, and it freezes at — 7·3° C. to give reddish-brown crystals.* At ordinary temperatures bromine rapidly evaporates if exposed in an open vessel.

Bromine is soluble in a number of liquids giving reddish-brown solutions; the chief are—water, alcohol, ether, acetic acid, carbon disulphide, and chloroform. At 0° C. 1 grm. of water dissolves 0·036 grm. of bromine; the solubility in the other liquids mentioned is considerably greater.

Exp. 46. Test the solubility of bromine in some or all of the above liquids (using the bromine you prepared in the last experiment). By adding the bromine drop by drop to equal volumes of each of the liquids (say 5 c.cm.), shaking up after each addition, and noting when further solution ceases (as shown by the bromine remaining undissolved at the bottom of the liquid), a rough comparison of its solubility in the different solvents can be made.

Bromine, like chlorine, contains two atoms in its gaseous molecule, except at high temperature, when partial dissociation into free atoms takes place. The dissociation is, however, much more complete with bromine than with chlorine.

As regards its chemical properties, bromine behaves like chlorine, but is generally much less active. Thus, many metals and non-metals combine readily with bromine, some (*e.g.* arsenic) with evolution of so much heat that they take fire. The action of bromine on phosphorus is, indeed, so violent that it is advisable to moderate it by dissolving the bromine in three times its volume of carbon disulphide.

Bromine and hydrogen do not combine directly at ordinary

* This is a method of obtaining pure bromine. Freeze the liquid, decant, melt the crystals, and freeze again, etc.

temperatures, but combination can be brought about by the application of heat, *e.g.* by passing the mixed gases through a red-hot tube. A solution of bromine in water (called *bromine water*) gradually decomposes in sunlight with evolution of oxygen and formation of hydrobromic acid—

$$2\,Br_2 + 2\,H_2O = 4\,HBr + O_2.$$

The decomposition is, however, much slower than with chlorine.

As we should expect from what has just been said, bromine water acts as a mild oxidising agent and exhibits feeble bleaching properties, its action being explained exactly as in the case of chlorine. It is much used as an oxidising agent in analytical chemistry. Bromine readily attacks organic substances such as starch and the skin, turning them *yellow*.

Exp. 47. Add a drop of bromine water to some starch and note the yellow colour developed.

As already stated in dealing with the manufacture of bromine, this element is displaced from its compounds with metals by chlorine. The following experiment should be performed to illustrate this.

Exp. 48. Add some chlorine water to a solution of potassium bromide : note the red colour developed. Shake up the liquid with a little carbon disulphide. The bromine dissolves in it and the red solution collects at the bottom of the vessel.

Bromine is used in photography, in medicine as a disinfectant, and as an oxidising agent in many chemical reactions.

Action of Bromine on the Alkalies.—Bromine reacts with a solution of sodium hydroxide like chlorine (see § 154). In the cold sodium hypobromite is produced in solution, but readily changes into sodium bromate on heating—

$$Br_2 + NaOH = NaOBr + NaBr + H_2O$$
$$3\,NaOBr = 2\,NaBr + NaBrO_3.$$

Bromine Hydrate.—Bromine combines with water at low temperatures, forming a compound, $Br_2 \cdot 10\,H_2O$, corresponding to chlorine hydrate.

Iodine, I_2.

164. History.—Iodine was discovered by Courtois in 1812. He obtained it by heating with sulphuric acid the mother liquors remaining after the crystallisation of sodium carbonate from the ash of marine plants. Gay-Lussac investigated its properties and named it Iodine on account of its violet vapour.

165. Occurrence.—Iodine is not found free in nature, but its compounds with the metals potassium, sodium, magnesium, and calcium are widely distributed, though they do not occur in large quantity at any one place. Thus sea water and the plants and animals which inhabit the sea, notably sea-weed, contain small quantities of iodides, as also do many mineral waters. The crude sodium nitrate (caliche), found in such abundance in Chile and Peru, contains small quantities of sodium iodate, and this is now the chief source of the element.

166. Preparation.—In the laboratory iodine is prepared in a similar manner to bromine, namely, by heating potassium or sodium iodide with manganese dioxide and strong sulphuric acid—

$$2\,KI + 3\,H_2SO_4 + MnO_2 = 2\,KHSO_4 + MnSO_4 + 2\,H_2O + I_2.$$

This method is, as we have seen, a general one for the preparation of the halogens, except fluorine, and the reaction may be represented thus—

$$2\,XR + 3\,H_2SO_4 + MnO_2 = 2\,XHSO_4 + MnSO_4 + 2\,H_2O + R_2$$

where X = K or Na and R = Cl, Br or I.

Exp. 49. Prepare iodine by following the directions in Exp. 45, using potassium iodide in place of potassium bromide. The same apparatus should be used, but it will not be necessary to cool the receiver by cold water. Some of the iodine will probably condense in the neck of the retort; it can be driven into the receiver by gently warming with a Bunsen burner.

167. Manufacture.—As stated above, the sodium iodate ($NaIO_3$) present in caliche is the chief source of iodine. The mineral is treated with water and then crystallised, when the

bulk of the sodium nitrate separates, and the sodium iodate being much more soluble remains in the mother liquor. This mother liquor is treated with sodium hydrogen sulphite solution which precipitates the iodine—

$$2\,NaIO_3 + 5\,NaHSO_3 = 3\,NaHSO_4 + 2\,Na_2SO_4 + I_2 + H_2O.$$

The iodine is allowed to settle out, washed and pressed into cakes, and finally resublimed at as low a temperature as possible.

In Scotland, iodine is extracted from deep-sea weed, which contains from about 0·27 to 0·47 per cent. of iodine. The best process in use for obtaining this iodine is the following :—

The weed, which must after collecting be kept dry until used, is boiled with sodium carbonate and filtered : the filtrate is treated with hydrochloric acid, and again filtered, the filtrate in this case being neutralised with caustic soda, evaporated to dryness, and carbonised. The two filtrations have separated two organic bodies which resemble cellulose and albumen respectively, and have found several useful applications. The carbonised residue is treated with warm water, and evaporated until all the less soluble salts (chiefly potassium sulphate and chloride) have crystallised out. The mother liquor is treated with a little sulphuric acid to decompose sulphides and sulphites. It is then distilled with manganese dioxide and sulphuric acid, the former being added in small quantities at a time. Iodine distils over and is purified by resubliming.

168. Properties.—Iodine is a lustrous crystalline black solid of specific gravity 4·94. It melts at 113° C., and boils at 184° C., forming a deep violet vapour ; at ordinary temperatures, however, iodine slowly undergoes vaporisation. The density of iodine vapour is very high, being about eight and a half times as great as that of air, and 126 times that of hydrogen. This corresponds to a molecular weight of $2 \times 126 = 252$, which is about twice the atomic weight of iodine, so that the gaseous molecule of iodine contains two atoms. This is only true up to 450° C., however, for above this temperature the density gradually falls, till at 1,500° C.

its value is reduced by nearly one-half, showing that most of the molecules have been broken down into single atoms—

$$I_2 = I + I.$$

We have seen that chlorine and bromine behave in a similar manner, but the decomposition is much less complete than in the case of iodine. Since bromine is decomposed to a greater extent than chlorine, we have here another property which follows the order of the atomic weights of the three elements.

Iodine is only slightly soluble in water, 100 grm. of which dissolve 0·02 grm. of the element, but many other liquids dissolve it in much greater quantity. These solvents may be divided into two classes, according as the colour of the solution they produce is reddish-brown or violet; to the former class belong water, potassium iodide, alcohol, and ether; and to the latter, carbon disulphide, chloroform, and liquid hydrocarbons.

Exp. 50. Introduce a crystal of iodine into about 5 c.cm. of each of the liquids mentioned above (as an example of a liquid hydrocarbon you can use benzene). You will notice that in all these liquids, except water, a deeply-coloured solution is rapidly formed; the water is only coloured slightly brown.

Observe that the colours of the different solutions correspond with those stated above.

169. Preparation of Pure Iodine.—Advantage is taken of the solubility of iodine in a solution of potassium iodide in preparing *pure iodine*. Commercial iodine, which may contain chlorine and bromine, is dissolved in a strong solution of potassium iodide. The liquid is then poured into a large volume of water, when most of the iodine is precipitated because the solution becomes too dilute to keep it dissolved. Any chlorine or bromine originally present in the iodine remain in solution as potassium chloride or potassium bromide respectively. The iodine is filtered off, washed with water, dried, and sublimed.

Exp. 51. Dissolve as much iodine as you can in about 5 c.cm. of a strong solution of potassium iodide. Pour this into a beaker of water, when you will find that the iodine separates out as a black precipitate.

170. Action of Iodine on other Elements.—Iodine is not nearly such an active substance as the other halogens, but it nevertheless combines directly with many elements, both metals and non-metals, often, indeed, without the application of heat. For example, mercury and iodine will unite on merely rubbing them together; again, on bringing together phosphorus and iodine, the phosphorus first melts and then combination takes place with so much energy that the mixture bursts into flame. When antimony powder is thrown into iodine vapour it takes fire; and on heating potassium and iodine together they unite with explosive violence.

Hydrogen and iodine combine directly with even greater difficulty than hydrogen and bromine, the temperature necessary being much higher; the combination is facilitated by the presence of spongy platinum, which acts as a catalytic agent. As we should expect from this, iodine in the presence of water has no bleaching properties.

Iodine is a mild oxidising agent. Thus it oxidises sulphuretted oxygen to sulphur,

$$I_2 + H_2S = 2\,HI + S.$$

and it converts sodium thiosulphate into sodium tetrathionate,

$$I_2 + Na_2S_2O_3 = 2\,NaI + Na_2S_4O_6,$$

a fact which is used for the estimation of iodine.

171. Displacement of Iodine from its Salts.—Just as chlorine displaces bromine from its compounds, illustrating thereby its greater activity, so both chlorine and bromine will displace iodine from its compounds. For example, on treating potassium iodide with either chlorine or bromine, free iodine is liberated—

$$2\,KI + Cl_2 = 2\,KCl + I_2.$$
$$2\,KI + Br_2 = 2\,KBr + I_2.$$

Exp. 52. Add a few drops of chlorine water to about 10 c.cm. of a solution of potassium iodide. The solution will turn reddish-brown, owing to the liberated iodine dissolving in the excess of potassium iodide. Now shake up with a little carbon disulphide. This will dissolve out the iodine, forming a violet solution which will collect at the bottom of the vessel.

A similar experiment may be performed using bromine water in place of chlorine water.

172. The "Starch Test" for Iodine.—Iodine forms a very characteristic blue compound with starch. On heating, the compound is decomposed and the colour disappears, but on cooling recombination takes place and the colour reappears.

Exp. 53. Shake a very little starch in a test-tube of cold water and boil well; add a few drops of a solution of iodine in potassium iodide; a blue colour is formed. Boil the blue solution, and the blue colour disappears, reappearing on cooling.

Action of Iodine on the Alkalies.—Iodine dissolves in cold caustic soda to give sodium hypoiodite and sodium iodide—

$$I_2 + 2\,NaOH = NaIO + NaI + H_2O.$$

However, this reaction is reversible and even in cold solutions the sodium hypoiodite is slowly transformed into the iodate—

$$3\,NaIO = 2\,NaI + NaIO_3.$$

173. Uses.—Iodine is largely employed in medicine for taking down glandular swellings. It was at one time thought that the iodine must be applied in the free state, and an alcoholic solution was (and still is) used; it has recently been found, however, that potassium iodide is quite as effective, and as it does not leave any stain on the skin its employment is preferable.

Iodine in the form of potassium iodide is also used as a tonic. Further, a compound of iodine with carbon and hydrogen, called iodoform (CHI_3), finds wide application as an antiseptic. Iodine is used for photographic preparations, in the preparation of dyes, and in organic chemistry.

174. Compounds of the Halogens with Each Other.—The halogens form several unstable compounds with each other, viz. BrF_3, IF_5, ICl, ICl_3, IBr, IBr_3. The existence of the last two compounds has not been clearly established.

Iodine Monochloride, ICl, is produced by the direct combination of its elements. It exists in two forms—

(*a*) A dark-red oily liquid resembling bromine, which on cooling is converted into a crystalline mass of dark-red plates melting at 14° C.;

(*b*) A dark-red crystalline solid, melting at 27° C. The crystals of this form are needle-shaped.

Iodine monochloride boils at 101° C. with slight decomposition. It is easily decomposed by water as follows :—

$$5\,ICl + 3\,H_2O = HIO_3 + 4\,I + 5\,HCl.$$

Iodine Trichloride, ICl_3, is prepared by the action of chlorine on the monochloride. It is a crystalline solid forming orange-yellow needles. On gently heating it dissociates into iodine monochloride and chlorine. It dissolves unchanged in a little water.

Iodine Bromide, IBr, is said to be produced by the direct combination of its elements. It has a crystalline form similar to iodine, and melts at 36° C.

Iodine Pentafluoride, IF_5, is obtained as a colourless liquid by the action of iodine on silver fluoride. It fumes in the air.

TABLE OF PHYSICAL AND CHEMICAL PROPERTIES OF THE HALOGENS.

Property.	Fluorine.	Chlorine.	Bromine.	Iodine.
Atomic weight ...	19	35·46	79·92	126·92
Atomic number ...	9	17	35	53
State of aggregation	gas	gas	liquid	solid
Colour of gas ...	pale yellow	greenish yellow	brownish	violet
Solubility (100 grm. water at 20°) dissolves grammes	decomposes water	0·72	3·2	0·03
Oxidis ng action...	strongest	very strong	strong	weak
Liquid form, B.Pt.	− 187°	− 33·6°	58·6°	183°
Solid „ M.Pt.	− 223°	− 102°	− 7·3°	+ 113°
Liquid „ Sp.gr.	1·14	1·55	3·19	5 (solid)
Fluorine compounds	—	ClF	BrF_3	IF_5
Halides	HF	HCl	HBr	HI

QUESTIONS.—CHAPTER XIV.

1. Draw up in tabular form a comparison between the halogen elements with regard to (*a*) their colour, (*b*) their solubility in water, (*c*) their action on water, (*d*) their affinity for hydrogen.

2. How was fluorine first prepared? Why is its isolation a matter of such great difficulty?

3. Write a short account of the history of chlorine.

4. Describe two processes by which chlorine is obtained on the large scale.

5. Describe experiments illustrating the great affinity of chlorine for hydrogen.

6. Describe experiments illustrating the *oxidising action* of chlorine.

7. Under what conditions does chlorine act as a bleaching agent?

8. Describe exactly how you would prepare bromine from potassium bromide, and give a sketch of the apparatus you would employ.

9. Give an account of the manufacture of bromine.

10. How is iodine obtained on the large scale?

11. Name some liquids which dissolve bromine and iodine, and state the colour of the solution produced in each case. Compare the action of these two halogens on starch.

12. How can *pure* iodine be conveniently prepared from commercial iodine?

13. What is the action of chlorine on solutions of sodium bromide, potassium iodide, and sulphuretted hydrogen respectively?

14. Describe any action which takes place when sulphur, phosphorus, carbon, silicon, and sulphuretted hydrogen are respectively brought into contact with fluorine and with iodine.

15. By what general method can the halogens (except fluorine) be prepared?

CHAPTER XV.

COMPOUNDS OF THE HALOGENS WITH HYDROGEN.

175. Introductory.—Hydrogen forms one compound with each of the halogens. These compounds are all gases at the ordinary temperature, except hydrogen fluoride, which is a very volatile liquid. They are all very soluble in water, producing strongly acid solutions. It will be convenient, for purposes of terminology, to use the terms *hydrogen fluoride*, *hydrogen chloride*, etc., for the gaseous acids (or anhydrous liquids), reserving the expressions *hydrofluoric acid*, *hydrochloric acid*, etc., for the aqueous solutions of the hydrides.

Hydrogen Fluoride or Hydrofluoric Acid, HF.

176. Preparation.—Hydrogen fluoride is obtained when a fluoride is gently heated with concentrated sulphuric acid; calcium fluoride (fluorspar) is generally used, a platinum or lead retort being employed, since glass is rapidly attacked by HF. The equation representing the reaction is—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF.$$

Pure hydrogen fluoride is obtained by heating potassium hydrogen fluoride, KHF_2, in a platinum or lead retort, provided with a delivery tube and receiver both of platinum, and both kept cool by a freezing mixture of calcium chloride and ice. The acid distils over and collects in the liquid form in the receiver. The KHF_2 is decomposed according to the equation—

$$KHF_2 = KF + HF.$$

177. Properties.—Hydrogen fluoride is a colourless mobile liquid which fumes strongly in moist air; it is very volatile; it boils at 19·4° C. and freezes at − 92° C. It is a very corrosive substance, readily attacking many metals and also organic substances such as the skin, cotton, silk, gums, etc. It also attacks glass, reacting with the silica present to produce silicon tetrafluoride (SiF_4), a gaseous substance.

$$4\,HF + SiO_2 = SiF_4 + 2\,H_2O.$$

This property may be illustrated as follows :—

Exp. 54. Coat a watch-glass with a thin layer of bees-wax or paraffin, and scratch on it some device. Next make a paste of a little powdered fluorspar and strong sulphuric acid in a leaden dish; warm gently, and expose the side of the watch-glass on which the device has been made to the fumes rising from the dish. The surface of the glass, where the wax or paraffin has been removed, will be acted upon, and on removing the wax or paraffin the device will be found to be etched clearly on the glass.

Perfectly dry hydrogen fluoride has no action on glass.

Hydrogen fluoride is very soluble in water, producing a strongly acid solution : as an acid, however, it is not so strong as the corresponding acids of the other halogens, viz.—HCl, HBr, HI. Hydrofluoric acid is kept in bottles of gutta-percha, cerasin, or paraffin wax, since these substances are not attacked by it. For transport lead vessels are used.

Hydrofluoric acid dissolves most metals very readily; copper and silver, neither of which is attacked at all by dilute hydrochloric acid, both dissolve in dilute hydrofluoric acid. Hydrofluoric acid is used extensively for etching glass, chiefly for making the graduations required in so many pieces of physical and chemical apparatus, *e.g.* thermometers and eudiometers. Sometimes the aqueous solution of the acid is used for this purpose, sometimes the gas. It also finds use in the spirit and brewing industry as an antiseptic, and in many processes to eliminate silica, *e.g.* from graphite and iron castings.

178. Fluorides.—The fluorides of the metals are usually prepared by the action of hydrofluoric acid on the metals or on their oxides, hydroxides, or carbonates. They exhibit

notable differences from the salts of the other haloid acids, for whereas silver fluoride is readily soluble in water, the silver salts of the other acids are insoluble; and whilst calcium, barium, and strontium fluorides are insoluble, the corresponding chlorides, bromides, and iodides are soluble. Again, the fluorides possess the power of uniting with hydrofluoric acid to produce *acid salts*, *e.g.* $KF \cdot HF$ or KHF_2; the other haloid salts do not exhibit this property.

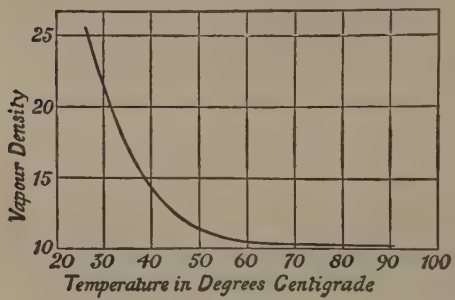


Fig. 32.

By the action of water on silicon tetrafluoride, an acid, *fluosilicic acid*, is obtained.

$$3\ SiF_4 + 4\ H_2O = 2\ H_2SiF_6 + Si(OH)_4.$$

This acid gives rise to a series of salts called silicofluorides or fluosilicates, *e.g.* K_2SiF_6 potassium fluosilicate.

Fluorine resembles oxygen in forming a compound in which fluorine is combined both with a metal and a non-metal, *e.g.* KBF_4, potassium borifluoride; and in other compounds where the boron is replaced by titanium, lead, etc.

179. Composition of Hydrogen Fluoride.—The vapour density of hydrogen fluoride when taken at 26·4° C. is found to be 25·5 (H = 1), but as the temperature rises the value falls rapidly till 60° C. is reached; above this temperature the decrease is much less rapid, and at about 90° C. the value becomes constant, being a little over 10. This corresponds to a molecular weight $2 \times 10 = 20$, which agrees with the simple formula HF (H + F = 1 + 19 = 20), so that above 90° C. hydrogen fluoride consists of simple molecules.

As the temperature falls below 90° C., however, the simple molecules gradually unite to form complex molecules corresponding to the gradual increase in density. Thus at 32° C. the density is about 20, corresponding to a molecular weight 40. This would agree with a formula H_2F_2, but there is no evidence to show that at this temperature all the molecules consist of H_2F_2. All we can say is that the *mean* composition at this point corresponds to H_2F_2; the actual molecules present may be partly HF, partly H_2F_2, and partly H_3F_3. Below 32° the density rises still further, so that *some* molecules more complex than H_2F_2 *must* exist.

The best way to represent the gas below 90° C. is to say that it consists of a mixture of molecules H_xF_x, H_yF_y, etc., where x, y, etc., are unknown. The change in composition with change in temperature is best represented by a curve (Fig. 32) in which temperatures are taken as abscissae and densities as ordinates.

Hydrogen Chloride or Hydrochloric Acid, HCl.

180. History.—The mixture of hydrochloric and nitric acids, called *aqua regia*, was known to the Arabian alchemists about the eighth century. Aqueous hydrochloric acid itself, under the name *spiritus salis*, is first mentioned in the works of the monk Basil Valentine who lived about 1400. From its great solubility in water, it was natural that *gaseous* hydrochloric acid was not discovered until Priestley, about 1770, began to collect gases over mercury instead of over water—a method which led in rapid succession to the discovery of gaseous ammonia, hydrochloric acid, silicon tetrafluoride, and sulphur dioxide.

Priestley called hydrochloric acid gas *marine acid air*, because it was obtained from sea salt. It was also called *muriatic acid*, that is an oxygen compound of *murium* or chlorine. Davy first showed that muriatic acid was a hydrogen compound of chlorine, and therefore hydrochloric acid.

181. Occurrence.—Hydrogen chloride is one of the gaseous products of the eruption of volcanoes, and is found as a normal constituent of the gastric juice of mammals.

182. Preparation.—Hydrogen chloride is most conveniently prepared by the action of concentrated sulphuric acid on common salt (sodium chloride).* The gas is evolved in the cold with effervescence, but much more rapidly on gently heating; the following reaction takes place :—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

Hydrogen chloride cannot be collected over water, in which it is very soluble; it may, however, be collected by downward displacement of air or over mercury.

Exp. 55. The apparatus required for the preparation of hydrogen chloride is sketched in Fig. 33. Introduce into the flask some common salt, and fill the wash-bottle about one-third full of concentrated sulphuric acid. Connect up the apparatus as shown and pour concentrated sulphuric acid slowly down the thistle funnel till it just covers the salt. Warm *gently* and collect the gas, which is dried by the sulphuric acid in the wash-bottle, in glass cylinders or other vessels as required. If the gas is wanted *pure* and *quite dry* it should be passed through two sulphuric acid wash-bottles and collected over mercury.

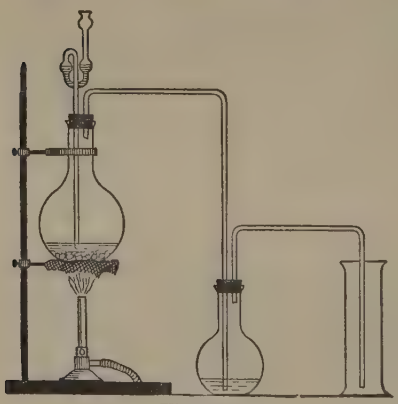


Fig. 33.

183. Properties.—Hydrogen chloride is a colourless gas which fumes in moist air and has a strongly irritant action on the mucous membrane. Its specific gravity is 18·2 (H = 1), and it is therefore about $1\frac{1}{4}$ times as heavy as air.

Hydrogen chloride is extremely soluble in water, 1 c.cm. of which at 0° C. dissolves 503 c.cm. of the gas, and at ordinary temperatures about 450 c.cm. The solution of the gas is accompanied by a considerable evolution of heat, and there

* All chlorides except silver chloride and mercurous chloride yield hydrochloric acid when heated with sulphuric acid.

is also an increase in the volume of the liquid. The following experiment illustrates in a striking manner the great solubility of hydrogen chloride.

Exp. 56. Fill a large dry flask, of at least two or three litres content, with hydrogen chloride gas by displacement. Fit it with an india-rubber cork, through which passes a tube with stopcock, and drawn out into a jet as shown in Fig. 34. Dip the extreme end of the tube into water and open the stopcock.

Under these conditions the gas at first only comes into contact with the water very slowly by a process of diffusion, and it is desirable to bring about contact with a larger surface of water by cooling the flask; this may be done by pouring a few drops of ether over its surface. When the water reaches the top of the tube and overflows into the flask, the first few c.cm. of water dissolve the whole of the gas, and the rest of the water rushes up through the tube with great force to fill the vacuum in the flask.

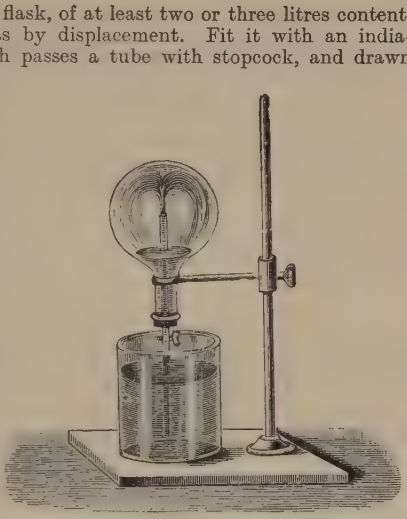


Fig. 34.

Hydrogen chloride is not combustible nor is it a supporter of combustion.

Exp. 57. Introduce a lighted taper into a jar of the gas. The flame is extinguished and the gas does not burn. Try similar experiments with burning sulphur and phosphorus; these are also extinguished.

The gas attacks many metals, especially when heated, with liberation of hydrogen and formation of a chloride of the metal.

Exp. 58. Place some zinc in a short piece of combustion tubing; heat it, and pass hydrogen chloride over it. Collect the gas given off over water. Test it with a lighted taper; it is hydrogen. The white residue left in the tube is zinc chloride, $ZnCl_2$—

$$Zn + 2\,HCl = ZnCl_2 + H_2.$$

Similar experiments may be performed with other metals, *e.g.* iron and magnesium.

Hydrogen chloride also reacts with many metallic oxides, especially when heated. If the oxide is a *basic oxide*, water and a chloride of the metal are the products; an experiment (Exp. 27) illustrating this has already been performed; *peroxides*, on the other hand, give rise to free chlorine, together with water and a chloride of the metal.

Exp. 59. Proceed exactly as described in Exp. 27, using manganese dioxide instead of lime. Test the issuing gas, which is yellowish-green in colour, with moist litmus paper; it is bleached. The gas is chlorine.

The equation representing the change which takes place is the same as that we have already met with in the preparation of chlorine, viz.—

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2.$$

When the gas is brought into contact with ammonia gas direct combination takes place with formation of dense white fumes of ammonium chloride (NH_4Cl) unless the gases are *quite dry*—

$$NH_3 + HCl = NH_4Cl.$$

184. Analytical Proof of the Composition of Hydrogen Chloride.—We can prove that hydrogen chloride contains half its volume of hydrogen by acting on it with metallic sodium, when the chlorine is extracted and combines with the sodium forming sodium chloride—

$$2\,HCl + 2\,Na = 2\,NaCl + H_2.$$

The sodium is most conveniently used in the from of a solution in mercury (called *sodium amalgam*), and the experiment may be carried out as follows :—

Fig. 35.

Exp. 60. About 50 c.cm. of hydrogen chloride are introduced into the closed limb of a bent eudiometer tube previously filled with mercury (Fig. 35). The levels of mercury in the two limbs are made equal by running mercury out of the tap or pouring more into the open limb, and the volume of gas is measured.

Mercury is now allowed to run out of the tap till very little is left in the open limb, and the latter is filled up with liquid sodium amalgam. The open end is then closed by the thumb and the hydrogen chloride transferred to the other limb by inverting and suitably manipulating the apparatus. The eudiometer is now restored to its normal position and then again inverted so as to bring the gas intimately in contact with the amalgam. Finally the gas is restored to the closed limb, and liquid is run out through the tap till the levels in the two limbs are equal.

The volume of gas which remains will be found to be half that originally taken, and it may be proved to be hydrogen by the usual tests.

To prove that the volumes of chlorine and hydrogen which combine to form hydrogen chloride are equal, an aqueous solution of the gas may be submitted to electrolysis.

Exp. 61. The experiment is carried out in the apparatus shown in Fig. 36, which consists of a three-limbed glass vessel, the two side limbs being provided with stopcocks and the central one with a funnel. At the base of the side limbs are the electrodes which are connected to the poles of a battery. The negative electrode, at which hydrogen is evolved, may be made of platinum, but since chlorine acts on platinum, the positive electrode must be made of gas carbon.

Strong hydrochloric acid is introduced through the funnel till the side tubes are full, and an electric current is passed through the liquid with the stopcocks open till the liquid in the limb containing the positive electrode is saturated with chlorine; the hydrogen liberated in the other limb being almost insoluble escapes meanwhile through the open stopcock. The stopcocks are now closed, and the gases will be found to collect in equal volumes in the two limbs. Their identity may be proved by the usual tests.

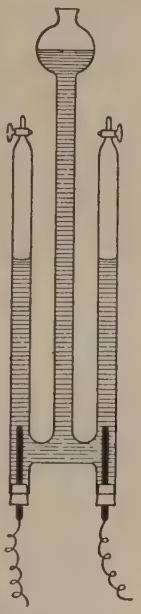


Fig. 36.

From the results of these two experiments it follows that two volumes of hydrogen chloride consists of one volume of hydrogen and one volume of chlorine.

185. Synthetical Proof of the Composition of Hydrogen Chloride.—The composition of hydrogen chloride may be conveniently investigated synthetically by means of the following experiment :—

Exp. 62.—Hydrochloric acid is electrolysed in the vessel A, Fig. 37 (using gas carbon electrodes), and when the liquid is saturated with chlorine a stout glass tube, B, provided with a stopcock at each end, is attached to the delivery tube of A. The other end of B is connected with a bottle containing fragments of pumice stone moistened with caustic soda solution to absorb the chlorine as it escapes. The stopcocks are opened and the mixture of hydrogen and chlorine in equal volumes generated in A is passed through B for some time so that all the air is driven out.* The stopcocks are then closed and the tube disconnected.

On opening one of the stopcocks under a solution of potassium iodide the chlorine reacts with the KI, liberating iodine, and if the experiment has been conducted properly the liquid will rise just half-way up the tube, showing that the chlorine and hydrogen are present in equal volumes.

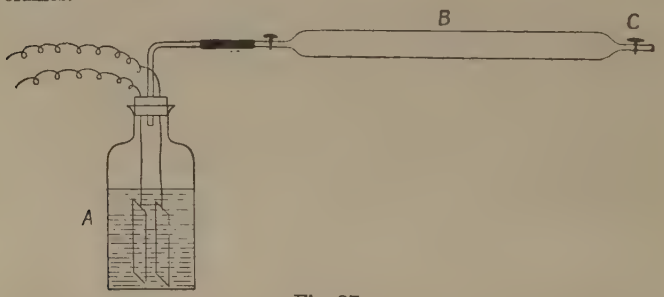


Fig. 37.

The tube is now cleaned out and again filled with the electrolytic mixture of hydrogen and chlorine. The stopcocks are again closed and the tube is disconnected and exposed to the action of the rays from burning magnesium wire (the face should be protected by a thick sheet of glass to avoid accident in case the tube explodes). The gases combine with explosion.

The tube is allowed to become quite cold and one of the stopcocks is then opened under mercury. No gas escapes and the mercury does not rise in the tube, showing that the volume of hydrochloric acid is exactly the same as that of the mixed gases from which it was formed.

The stopcock is now closed and opened again under water; the water rushes up and fills the whole tube, the hydrogen chloride formed dissolving completely. This shows that the whole of the gases have combined to form hydrogen chloride.

We thus arrive at the same composition for hydrogen chloride by synthesis as by analysis.

* This must be done in the dark to prevent combination of the gases.

The synthetical proof of the composition of hydrogen chloride by weight is interesting. A known weight of hydrogen is burnt in a known weight of chlorine, and the weight of hydrogen chloride is determined. This experiment also gives the equivalent weight of chlorine and its atomic weight, as its valency is unity.

186. Liquid Hydrogen Chloride.—Hydrogen chloride condenses to a colourless liquid under a pressure of 40 atmospheres at 10° C.; the liquid boils under ordinary pressure at — 83° C. and solidifies at — 115° C. Liquid hydrogen chloride is without action on most metals, *e.g.* magnesium and zinc, nor does it act on metallic oxides, such as lime, or on anhydrous carbonates; it is therefore an inactive substance, and does not even redden dry litmus paper.

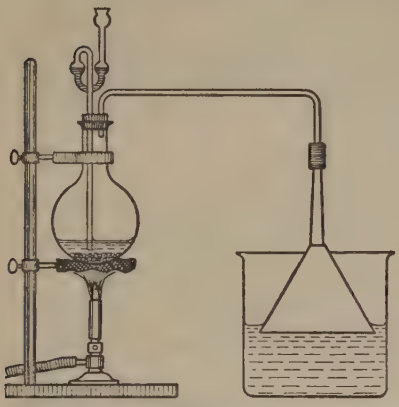


Fig. 38.

187. Preparation of Aqueous Hydrochloric Acid.—A solution of hydrogen chloride in water, commonly called hydrochloric acid (also known as "spirits of salts" and "muriatic acid"), may be conveniently prepared in the following manner :—

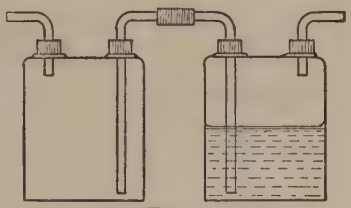


Fig. 39.

Exp. 63. Generate hydrogen chloride in the flask A (Fig. 38), as described in Exp. 55, and use some arrangement to prevent "sucking back," as the gas is very soluble. Two useful devices are shown in Fig. 38, which is an inverted funnel, and Fig. 39 which consists of two wash bottles arranged as a

so-called "Volhard" gas trap. The hydrogen chloride is absorbed by the water, and if the process is continued long enough the solution finally becomes saturated, when it contains from 40 to 45 per cent. of HCl.

188. Properties of Aqueous Hydrochloric Acid.—Hydrochloric acid is the strongest acid known; it is very corrosive, being much more active than the gas.

Action on Metals.—Many metals are attacked by hydrochloric acid, some readily by the dilute acid, others only by the hot concentrated acid. In all cases the products are a chloride of the metal and hydrogen. The following table gives a *résumé* of the action of the acid on a number of common metals under different conditions.

ACTION OF HYDROCHLORIC ACID ON METALS.

Metal.	Cold dilute HCl.	Hot concen. HCl.	Product.
Zinc	Dissolves readily	Dissolves readily	$ZnCl_2$
Magnesium	,, ,,	,, ,,	$MgCl_2$
Iron	,, ,,	,, ,,	$FeCl_2$
Aluminium	,, rather slowly	,, ,,	$AlCl_3$
Tin	,, slowly	,, ,,	$SnCl_2$
Copper ...	Insoluble*	,, slowly	Cu_2Cl_2
Lead... ...	,,	,, very slowly	$PbCl_2$
Mercury ...	,,	Insoluble	Nil
Silver ...	,,	Dissolves slowly	AgCl
Gold ...	,,	Insoluble	Nil
Platinum .	,,	,,	Nil

189. Chlorides.—The chlorides of the metals may be produced by the direct union of the metals with chlorine, or by the action of hydrochloric acid on the metals (in some cases) or on their oxides, hydroxides, or carbonates. Zinc

* Copper is slowly attacked by dilute hydrochloric acid *in the presence of air*; the same remark applies to lead—

$$2\,Cu + 4\,HCl + O_2 = 2\,CuCl_2 + 2\,H_2O.$$

(from the air).

chloride, $ZnCl_2$, for instance, may be produced by any of these methods as shown in the following equations :—

$$Zn + Cl_2 = ZnCl_2.$$
$$Zn + 2\,HCl = ZnCl_2 + H_2.$$
$$ZnO + 2\,HCl = ZnCl_2 + H_2O.$$
$$Zn(OH)_2 + 2\,HCl = ZnCl_2 + 2\,H_2O.$$
$$ZnCO_3 + 2\,HCl = ZnCl_2 + H_2O + CO_2.$$

In the case of those metals forming two or more chlorides, direct union of the metal and chlorine generally yields the higher chloride, *e.g.*—

$$2\,Fe + 3\,Cl_2 = Fe_2Cl_6$$
$$Sn + 2\,Cl_2 = SnCl_4.$$

When a metal forms an *insoluble* chloride a special method of preparation is applicable, viz. the addition of a solution of a soluble chloride to a solution of soluble salt of the metal; double decomposition takes place, the insoluble chloride being precipitated. Silver chloride is, for example, precipitated when a solution of silver nitrate, $AgNO_3$, is added to a solution of calcium chloride, $CaCl_2$.

$$CaCl_2 + 2\,AgNO_3 = \underset{\text{Calcium nitrate.}}{Ca(NO_3)_2} + 2\,\underset{\text{Silver chloride.}}{AgCl}.$$

Most metallic chlorides are easily soluble in water; the only insoluble ones are mercurous chloride (calomel), Hg_2Cl_2, cuprous chloride, Cu_2Cl_2, lead chloride, $PbCl_2$ (which is sparingly soluble in cold water and readily in hot) and aurous chloride, AuCl, in addition to silver chloride already referred to. The metallic chlorides, with the exception of those of Sb, Bi, As, are stable in aqueous solution.

Some chlorides decompose on heating and give either the elements or a lower chloride—

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$PtCl_4 = Pt + 2\,Cl_2.$$

The chlorides of the non-metals are fairly stable bodies, but in most cases are hydrolysed by water.

$$PCl_3 + 3\,H_2O = H_3PO_3 + 3\,HCl$$
$$2\,S_2Cl_2 + 3\,H_2O = H_2SO_3 + 4\,HCl + 3\,S.$$

190. Action of Heat on Hydrochloric Acid.—When a strong solution of hydrochloric acid is distilled it at first loses hydrochloric acid much faster than water, *i.e.* it becomes weaker. This goes on till the percentage of HCl is 20·24, when the liquid distils over unchanged in composition. Similarly, if a solution containing less than 20·24 per cent. of hydrochloric acid is distilled it loses water faster than HCl till the percentage of HCl is 20·24, when the liquid again distils unchanged. The boiling-point of hydrochloric acid of this particular strength is 110° C.

It must be noted that the acid which distils unchanged only has the composition and boiling-point stated when the *pressure is normal*; for any other pressure, the composition and boiling-point of the liquid which distils unchanged have different values, which, however, are constant for each particular pressure.

When hydrogen chloride dissolves in water a large amount of heat is set free, which is probably in part due to the formation of hydrates, three of which have been isolated, viz. $HCl.H_2O$, $HCl.2\,H_2O$, and $HCl.3\,H_2O$.

191. Manufacture of Hydrochloric Acid.—(1) *The Salt Cake Process.*—Hydrochloric acid is manufactured in enormous quantities as a by-product in the conversion of common salt into salt-cake (sodium sulphate, Na_2SO_4) by the action of strong sulphuric acid. The first part of the process is performed at a gentle heat and the reaction is the same as that given in § 182. The mixture is then heated to a *much higher* temperature, when the acid sodium sulphate reacts with another molecule of sodium chloride, producing normal sodium sulphate and hydrochloric acid according to the equation—

$$NaCl + \underset{\text{Acid sodium sulphate.}}{NaHSO_4} = \underset{\text{Normal sodium sulphate.}}{Na_2SO_4} + HCl.$$

The gas is passed up stone towers filled with lumps of coke, over which a slow stream of water flows; the hydrochloric acid is absorbed, and the aqueous solution runs away from the bottom of the tower into suitable receivers.

(2) *The Synthetic Process.*—In some places hydrochloric acid is made synthetically. The gaseous products from the electrolytic manufacture of caustic soda are hydrogen and chlorine. The hydrogen is burnt in chlorine, and condensation takes place in water in the ordinary earthenware apparatus.

(3) *The Hargreaves Process.*—This depends on the direct action of sulphur dioxide on common salt in the presence of steam and atmospheric oxygen—

$$2\,NaCl + SO_2 + H_2O + O = Na_2SO_4 + 2\,HCl.$$

As the reaction proceeds heat is developed and is sufficient to make the operation continuous. Thus fuel is saved, and sulphuric acid is not required, and therefore leaden chambers are not necessary.

Impurities in the Commercial Acid.—The chief impurities in commercial hydrochloric acid are ferric chloride, free chlorine, sulphuric acid, arsenious chloride, and sulphurous acid. The ferric chloride is the principal cause of the yellow colour usually noticeable in the commercial acid.

192. Uses of Hydrochloric Acid.—The most important use of hydrochloric acid is in the manufacture of chlorine. It is also used in dyeing and calico printing, in obtaining phosphates from bones, and in manufacturing colours. Its employment in the manufacture of metallic chlorides is also of importance, and it is very extensively used in chemical laboratories for a variety of purposes.

Hydrogen Bromide or Hydrobromic Acid, HBr.

193. Preparation.—Hydrogen bromide* can be prepared by the direct union of the elements. Combination of hydrogen and bromine vapour occurs fairly quickly at 250° C. The reaction is reversible, but if the hydrogen in excess is bubbled

* Discovered by Balard in 1830.

through liquid bromine and the gas then ignited, the forward reaction is practically complete.

$$H_2 + Br_2 \rightleftharpoons 2\,HBr.$$

In the presence of a catalyst, such as a spiral of platinum wire heated electrically, the gases unite practically quantitatively to form HBr, if hydrogen is in slight excess.

Hydrogen bromide cannot conveniently be prepared from potassium or sodium bromide in the same way that hydrogen chloride is prepared from common salt, because hydrogen bromide is a mild reducing agent, and the sulphuric acid is reduced to sulphurous acid and free bromine is liberated.

$$(1)\quad KBr + H_2SO_4 = KHSO_4 + HBr.$$

$$(2)\quad 2\,HBr + H_2SO_4 = Br_2 + SO_2 + 2\,H_2O.$$

This reducing action is a result of the instability of hydrogen bromide, which readily splits up into free hydrogen and bromine, the nascent hydrogen so produced then attacking the sulphuric acid thus—

$$2\,HBr = \underset{\text{Nascent.}}{2\,H} + Br_2.$$

$$2\,H + H_2SO_4 = 2\,H_2O + SO_2.$$

These two equations when combined give equation (2) above.

If, instead of sulphuric acid, an acid such as phosphoric acid, which is not so easily reduced, is employed, then the preparation can be carried on just as for hydrogen chloride.

The best method of preparation is to drop bromine on to a mixture of red phosphorus and water, when the following reactions take place :—

$$P_4 + 16\,H_2O + 10\,Br_2 = \underset{\text{Phosphoric acid.}}{4\,H_3PO_4} + 20\,HBr.$$

$$P_4 + 12\,H_2O + 6\,Br_2 = \underset{\text{Phosphorus acid.}}{4\,H_3PO_3} + 12\,HBr.$$

The particular reaction which preponderates depends on the relative quantities of phosphorus and bromine used. It may be supposed that these reactions take place in two stages, phosphorus and bromine first uniting to form phosphorus

pentabromide (PBr_5) and phosphorus tribromide (PBr_3), these compounds being immediately decomposed by water, thus—

$$P_4 + 10\ Br_2 = 4\ PBr_5.$$

$$P_4 + 6\ Br_2 = 4\ PBr_3.$$

$$PBr_5 + 4\ H_2O = H_3PO_4 + 5\ HBr.$$

$$PBr_3 + 3\ H_2O = H_3PO_3 + 3\ HBr.$$

The experiment is carried out as follows :—

A mixture of one part of red phosphorus and ten parts of water is introduced into a flask provided with a dropping funnel and delivery tube, as shown in Fig. 40. Ten parts of bromine are introduced into the funnel, and are *gradually* run into the flask; this is then *gently* warmed, and the hydrogen bromide is passed through a U-tube containing lumps of red phosphorus to remove bromine, the gas being collected by downward displacement or over mercury. Like hydrogen chloride, it cannot be collected over water, owing to its great solubility.

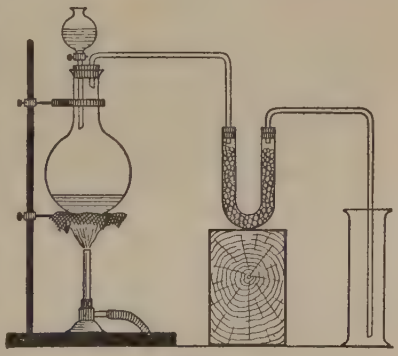


Fig. 40.

If an aqueous solution of the gas is required, the delivery tube from the U-tube in Fig. 40 should be connected to one of the arrangements suggested to prevent "sucking back" (see Figs. 38, 39).

Another simple method of preparing a solution of the gas is to pass sulphuretted hydrogen into bromine water, when the following change take place :—

$$2\ H_2S + 5\ Br_2 + 4\ H_2O = 10\ HBr + H_2SO_4 + S.$$

The precipitate of sulphur is filtered off and the liquid distilled, when hydrobromic acid passes over and sulphuric acid remains behind.

A very convenient method consists in passing sulphur dioxide from a siphon into bromine and ice and water. When the solution is a straw colour, *i.e.* when all the bromine has been converted to HBr, the solution is distilled and hydrobromic acid is obtained—

$$SO_2 + Br_2 + 2\,H_2O = 2\,HBr + H_2SO_4.$$

194. Properties.—Hydrogen bromide is a heavy colourless gas which, like hydrogen chloride, fumes in moist air, and has an irritating action on the mucous membrane. It condenses to a liquid which boils at — 69° C. and freezes at — 86° C. As already stated it is very soluble in water, producing a strongly acid solution which is very similar in properties to hydrochloric acid. By cooling the aqueous solution hydrates of HBr with from one to four molecules of water of crystallisation have been obtained.

On distilling hydrobromic acid at normal pressure it loses either water or acid, according as the solution contains less or more than 48·17 per cent. of HBr. The liquid of this composition distils over unchanged at 126° C. If the pressure is not normal there is a corresponding change in the composition and boiling-point of the liquid which distils unchanged.

Hydrogen bromide is incombustible, and is a non-supporter of combustion. It is immediately attacked by chlorine with liberation of free bromine and formation of hydrogen chloride—

$$2\,HBr + Cl_2 = 2\,HCl + Br_2.$$

Potassium, on the other hand, immediately liberates free hydrogen from hydrogen bromide, and forms potassium bromide—

$$2\,HBr + 2\,K = 2\,KBr + H_2.$$

195. Bromides.—The general methods of preparation of metallic bromides are similar to those given for metallic chlorides. Most metallic bromides are readily soluble in

water, the only common insoluble ones being silver bromide (AgBr), mercurous bromide (Hg_2Br_2), and lead bromide ($PbBr_2$), the last being sparingly soluble in cold water, but readily in hot water.

196. Composition of Hydrogen Bromide.—A convenient method of proving that hydrogen bromide contains half its volume of hydrogen consists in heating a small piece of sodium in the gas confined in a strong corked test-tube. When the reaction is complete, the tube is allowed to cool down to the atmospheric temperature and then uncorked under mercury in a trough, the residual volume of the gas is found to be half that originally taken.

The sodium has combined with the bromine to form sodium bromide, NaBr, and free hydrogen is liberated—

$$\underset{}{2\,Na} + \underset{2\text{ vols.}}{2\,HBr} = \underset{}{2\,NaBr} + \underset{1\text{ vol.}}{H_2}.$$

Applying Avogadro's hypothesis, which, it will be remembered, states that equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules, it follows that—

Two mol. of hydrogen bromide contain one mol. of hydrogen.
∴ ,, ,, ,, ,, two atoms ,,
∴ One mol. ,, ,, ,, contains one atom ,,

We do not yet know how many atoms of bromine are present in a molecule of hydrogen bromide; calling this x we can write the formula H_1Br_x. The simplest method of finding x is to determine the molecular weight of hydrogen bromide from its density. Now the relative density of hydrogen bromide (H = 1) is, in round numbers, 40·5, so its molecular weight is $2 \times 40{\cdot}5 = 81$. We have therefore—

Weight of a molecule of hydrogen bromide = 81
,, ,, hydrogen in a molecule of hydrogen bromide = 1
∴ ,, ,, bromine ,, ,, ,, ,, ,, = 80

But 80 is the atomic weight of bromine, and therefore a molecule of hydrogen bromide contains one atom of bromine, i.e. $x = 1$, and the formula of hydrogen bromide is HBr.

Hydrogen Iodide or Hydriodic Acid, HI.

197. Preparation.—Hydrogen and iodine* do not combine at ordinary temperatures, and only partially with rise of temperature as dissociation occurs of the HI produced. If a mixture of hydrogen and iodine vapour is passed over warm platinum sponge the action is practically complete—

$$H_2 + I_2 \rightleftharpoons 2\,HI.$$

Hydrogen iodide cannot be prepared by the action of sulphuric acid on potassium or sodium iodide for a reason similar to that given in the case of hydrogen bromide; hydrogen iodide is, in fact, much more unstable than hydrogen bromide, and the reaction goes almost entirely in accordance with the equation—

$$3\,H_2SO_4 + 2\,KI = 2\,KHSO_4 + SO_2 + 2\,H_2O + I_2.$$

If phosphoric acid is used, however, instead of sulphuric acid, hydrogen iodide is obtained free from iodine just as hydrogen bromide could be obtained free from bromine.

Hydrogen iodide is best prepared by a method similar to that used for hydrogen bromide, namely, by the mutual interaction of phosphorus, iodine, and water. The apparatus used is that shown in Fig. 40; since iodine is a solid it cannot be run in from a stoppered funnel as bromine is; instead, the iodine and amorphous phosphorus are mixed in the flask, and water is slowly run in from the funnel. Hydrogen iodide is evolved without heating, and, after passing through the U-tube containing amorphous phosphorus which removes iodine vapour, is collected by downward displacement or over mercury. When all the water has been added and the evolution of gas becomes slow, the flask may be gently warmed. The reaction which takes place is thus represented—

$$P_4 + 10\,I_2 + 16\,H_2O = 4\,H_3PO_4 + 20\,HI.$$

* Hydrogen iodide was discovered by Clément and Desormes in 1813.

If an aqueous solution of the gas (called hydriodic acid) is required, the absorption may be carried out by one of the methods described for HBr, as HI is also very soluble in water.

Another convenient method for the preparation of hydriodic acid is to pass sulphuretted hydrogen through water containing iodine in suspension, when the following change takes place :—

$$H_2S + I_2 = 2\,HI + S.$$

The hydriodic acid is separated from the precipitate of sulphur by distillation.

198. Properties.—Hydrogen iodide is a very heavy colourless gas which, like the other halogen hydrides, fumes strongly in moist air and has a very irritating action on the mucous membrane. Its great solubility in water has already been referred to ; the aqueous solution has strongly acid properties just like the solution of the other halogen hydrides. By cooling this solution, hydrates with $3\,H_2O$ and $4\,H_2O$ can be obtained. The behaviour of the solution on distillation is similar to that of hydrochloric acid and hydrobromic acid ; the liquid which distils unchanged at normal pressure contains 57·7 per cent. of hydrogen iodide and boils at 127° C., but at other pressures the composition and boiling-point have different values.

Hydrogen iodide is easily condensed to a liquid, a pressure of four atmospheres at 0° C. sufficing to bring this about ; the liquid boils at — 36° C. under normal pressure and freezes at — 51° C. Hydrogen iodide does not burn nor does it support combustion. As already pointed out, it is an unstable substance ; thus on exposing the gas to sunlight it slowly undergoes decomposition into its elements, and on heating it breaks up much more quickly. Also the aqueous solution gradually turns brown in sunlight owing to separation of free iodine.

On account of its instability and consequent tendency to produce nascent hydrogen, hydriodic acid is a powerful reducing agent, and is much used as such in organic chemistry ; we have already had occasion to notice its reducing action on strong sulphuric acid.

Hydrogen iodide, both in the gaseous state and in aqueous solution, is at once decomposed by chlorine or bromine with liberation of free iodine—

$$Br_2 + 2\,HI = 2\,HBr + I_2.$$

199. Iodides.—The iodides of the metals are produced by methods similar to those given for chlorides and bromides. The majority of the iodides dissolve easily in water, the chief insoluble ones being silver iodide (AgI), mercurous iodide (Hg_2I_2), mercuric iodide (HgI_2), cuprous iodide (Cu_2I_2), and lead iodide (PbI_2), the last being sparingly soluble in cold water and readily in hot.

200. Composition of Hydrogen Iodide.—By a method exactly similar to that described for hydrogen bromide (see § 196) it may be proved that hydrogen iodide contains half its volume of hydrogen. Its formula must therefore be H_1I_x, and we may prove that $x = 1$ just as we did for HBr, *i.e.* the formula for hydrogen iodide is HI.

201. Tests for the Halogen Acids and their Salts.—(1) A solution of silver nitrate, $AgNO_3$, when added to a solution of a halogen acid or haloid salt, gives with—

Hydrochloric acid, a white curdy precipitate of silver chloride, AgCl, soluble in ammonia, insoluble in nitric acid.

Hydrobromic acid, a pale yellow precipitate of silver bromide, AgBr, soluble in strong ammonia, insoluble in nitric acid.

Hydriodic acid, a yellow precipitate of silver iodide, AgI, insoluble in ammonia and in nitric acid.

Hydrofluoric acid gives no precipitate, as silver fluoride, AgF, is soluble.

(2) Free HCl, HBr, or HI, heated with manganese dioxide, or their salts, heated with manganese dioxide and sulphuric acid, evolve chlorine, bromine, and iodine respectively, and these elements are easily recognised by their colour, smell, and bleaching action.

(3) Chlorine water (which must not be in excess) added to a bromide or iodide liberates bromine or iodine, and on shaking

the liquid with carbon disulphide, the bromine imparts to it a red colour and the iodine a violet colour.

(4) Fluorides, when heated with concentrated sulphuric acid, evolve HF, which will etch glass.

TABLE OF PHYSICAL AND CHEMICAL PROPERTIES OF THE HALOID ACIDS.

Property.	Hydrogen Fluoride.	Hydrogen Chloride.	Hydrogen Bromide.	Hydrogen Iodide.
Molecular weight ...	20	36·46	80·93	127·93
Solubility in water ...	35·3%	42%	49%	57%
Specific gravity of saturated aqueous solution	1·15	1·21	1·49	1·7
Boiling point, aqueous solution	111° (43%)	110° (20%)	126° (47%)	127° (57%)
Heat of formation ...	+ 38·9	+ 22·0	+ 12·1	− 6·4
Liquid form (boiling-point)	19·4°	− 83·4°	− 67·1°	− 35·5° (4 atmos.)
Solid form (melting-point)	− 92·3°	− 113°	− 87·9°	− 50·8°
Dissociation commences at	—	1500°	800°	180°
Solubility of silver salt (at 20° in 100 grm. of water)	172	0·002	0·00008	0·000003
Solubility of calcium salt (as above) ...	0·002	42·7	58·8	67·6

QUESTIONS.—CHAPTER XV.

1. How is pure hydrogen fluoride prepared ?
2. Explain the action of hydrofluoric acid in etching glass.
3. Write a short account of the metallic fluorides.
4. Discuss the composition of the hydrogen fluoride molecule.
5. What do you know of the history of hydrochloric acid ?
6. How would you prepare *pure dry* hydrogen chloride ? Describe experiments which illustrate the chief properties of the gas.

7. State the changes which take place when very concentrated and very dilute hydrochloric acid are respectively boiled for some time in an open vessel.

8. On what evidence do we accept HCl as expressing the composition of hydrochloric acid gas ?

9. Compare the properties of liquid hydrogen chloride with those of an aqueous solution of the gas.

10. What is the action (if any) of (*a*) cold dilute, (*b*) hot strong hydrochloric acid on the following metals : (1) zinc, (2) aluminium, (3) gold, (4) lead, (5) copper, (6) tin ?

11. State briefly the general methods of preparing metallic chlorides, giving equations.

12. How is hydrochloric acid manufactured ? What are the chief impurities in the commercial acid ?

13. Enumerate the chief uses of hydrochloric acid.

14. Describe in detail the laboratory method of preparing an aqueous solution of hydrobromic acid.

15. How can it be proved that hydrogen bromide is represented by the formula HBr ?

16. Describe a method of preparing gaseous hydriodic acid. Compare and contrast hydriodic acid and hydrochloric acid.

CHAPTER XVI.

COMPOUNDS OF THE HALOGENS WITH OXYGEN.

Oxides of Chlorine.

202. Introductory.—Chlorine does not combine directly with oxygen, but three oxides of chlorine can be obtained by indirect methods, viz. *chlorine monoxide*, Cl_2O, *chlorine dioxide*, ClO_2, and *chlorine heptoxide*, Cl_2O_7. The first two of these compounds are gases and the last is a liquid; they are all very readily broken up into their elements. The oxides and acids are shown in the following table :—

Acid Anhydride or Oxide.		Acid.	
Chlorine monoxide,	Cl_2O	Hypochlorous acid,	$HClO$
Chlorine dioxide,	ClO_2	Chlorous acid,	$HClO_2$
(a " mixed " anhydride)		Chloric acid,	$HClO_3$
Chlorine heptoxide,	Cl_2O_7	Perchloric acid,	$HClO_4$

203. Chlorine Monoxide, Cl_2O,* is prepared by passing dry chlorine over dry freshly-precipitated and recently-ignited mercuric oxide, HgO, cooled to 0° C. by being contained in a glass tube immersed in ice—

$$2\,HgO + 2\,Cl_2 = HgO \cdot HgCl_2 + Cl_2O.$$

Mecuric oxychloride.

The gas is collected by downward displacement.

Chlorine monoxide is an orange-yellow explosive gas condensing to a dark brown liquid which boils at — 19° C., and which is much more explosive than the gas. It is readily soluble in

* Balard discovered chlorine monoxide in 1834 by this method.

water and enters into combination with it to form hypochlorous acid, HClO—

$$Cl_2O + H_2O = 2\,HClO.$$

We may, therefore, consider chlorine monoxide as hypochlorous acid *minus water*. Many other oxides combine with water to produce acids, and they may in a similar manner be regarded as consisting of the corresponding acids minus water. For this reason such oxides are called *anhydrides*, and chlorine monoxide is also called *hypochlorous anhydride*.

Chlorine monoxide, on account of its instability, possesses strong oxidising properties; thus phosphorus and sulphur are immediately converted by it into phosphorus pentoxide and sulphur trioxide respectively, and many organic substances, such as turpentine, readily take fire in the gas.

The *composition of the gas* can be shown by the method employed by Balard and Gay-Lussac. A known volume is exploded, and the volumes of chlorine and oxygen produced are measured. Thus two volumes of Cl_2O give on explosion 3 volumes of mixed gases; treatment with caustic potash solution, which dissolves the chlorine, leaves one volume of oxygen. Therefore, by Avogadro's hypothesis, 2 molecules of chlorine monoxide give 2 molecules of chlorine and 1 molecule of oxygen; hence the formula is Cl_2O.

204. Chlorine Dioxide or Chlorine Peroxide, ClO_2.—This can be obtained by the same method by which Davy, in 1815, discovered the gas, viz. by the action of concentrated sulphuric acid on potassium chlorate. The acid is placed in a small retort and cooled in a freezing mixture; potassium chlorate is then added in small quantities at a time. On now placing the retort in a saucepan of water and applying gentle heat chlorine dioxide is evolved and may be collected by downward displacement. The reaction which takes place is represented thus—

$$3\,KClO_3 + 2\,H_2SO_4 = KClO_4 + 2\,KHSO_4 + H_2O + 2\,ClO_2.$$

If concentrated hydrochloric acid is used instead of sulphuric acid a mixture of chlorine dioxide and chlorine is

evolved, which was considered by Davy to be a definite oxide of chlorine, and was called *euchlorine*—

$$8\,KClO_3 + 24\,HCl = 8\,KCl + 12\,H_2O + \underbrace{9\,Cl_2 + 6\,ClO_2}_{\text{Euchlorine.}}.$$

A method which is less dangerous is due to Bray : a mixture of carbon dioxide and chlorine peroxide is obtained when dilute sulphuric acid, potassium chlorate, and oxalic acid are heated to 60° C.—

$$2\,KClO_3 + H_2C_2O_4 + H_2SO_4 = K_2SO_4 + 2\,ClO_2 + 2\,CO_2 + 2\,H_2O.$$

Chlorine dioxide is a dark yellow gas which on passing through a U-tube immersed in a freezing mixture of ice and salt condenses to a red oily liquid boiling at 10° C. and freezes to orange-red crystals, melting at − 79° C. ; both the gas and the liquid are explosive. Chlorine dioxide dissolves in water to give a mixture of chloric and chlorous acids—

$$2\,ClO_2 + H_2O = HClO_3 + HClO_2.$$

On passing the gas into a solution of caustic potash it is absorbed with formation of a mixture of potassium chlorate and potassium chlorite—

$$2\,ClO_2 + 2\,KOH = \underset{\text{Potassium chlorate.}}{KClO_3} + \underset{\text{Potassium chlorite.}}{KClO_2} + H_2O.$$

Owing to its instability chlorine dioxide is a powerful oxidising agent, behaving towards phosphorus, sulphur, and organic substances just as chlorine monoxide does. The gas attacks mercury and so cannot be collected over that liquid.

The composition of the gas can be shown by a method similar to that given for chlorine monoxide.

205. Chlorine Heptoxide, Cl_2O_7.—This compound is obtained by adding anhydrous perchloric acid to phosphoric oxide cooled to − 10° C. The mixture is allowed to stand 24 hours at the same temperature, and is then heated to 82° C., when chlorine heptoxide distils over.

$$2\,HClO_4 + \underset{\text{Phosphorus pentoxide.}}{P_2O_5} = Cl_2O_7 + \underset{\text{Metaphosphoric acid.}}{2\,HPO_3}.$$

It is a colourless oil and very explosive. Chlorine heptoxide is not so powerful an oxidising agent as the other oxides of chlorine. It dissolves in water slowly to give perchloric acid.

$$Cl_2O_7 + H_2O = 2\,HClO_4.$$

Oxyacids of Chlorine.

206. The Four Oxyacids.—Chlorine forms four oxyacids, viz.—

Hypochlorous acid,	$HClO$.
Chlorous acid,	$HClO_2$.
Chloric acid,	$HClO_3$.
Perchloric acid,	$HClO_4$.

All these compounds are unstable; their stability, however, increases as the amount of oxygen increases, perchloric acid being the most stable. They all possess strong oxidising properties. Chlorous acid, $HClO_2$, has only recently (1912) been isolated, but salts derived from it, such as potassium chlorite, have been known for some time (see above under ClO_2).

207. Hypochlorous Acid, HClO.—This is a very unstable body, and can only be obtained in dilute aqueous solution, which may be prepared—

(1) By shaking up precipitated mercuric oxide and chlorine water—

$$HgO + 2\,Cl_2 + H_2O = HgCl_2 + 2\,HClO.$$

We have seen that in the *absence* of water Cl_2O is formed.

(2) By distilling a solution of a hypochlorite with *very dilute* nitric acid, or boric acid—

$$KClO + HNO_3 = HClO + KNO_3.$$

(3) Commercially, by the action of carbon dioxide on bleaching powder suspended in ice-cold water—

$$2\,CaOCl_2 + CO_2 + H_2O = CaCO_3 + CaCl_2 + 2\,HClO.$$

Owing to the ease with which it breaks up into hydrochloric acid and nascent oxygen, hypochlorous acid is a very strong oxidising agent—

$$HClO = HCl + \underset{\text{Nascent.}}{O}.$$

Its powerful bleaching properties are an illustration of this oxidising action. On exposure to light, solutions of hypochlorous acid decompose as above, and also as follows :—

$$3\,HClO = 2\,HCl + HClO_3;$$

and by the action of hydrochloric acid chlorine is liberated—

$$HCl + HClO \rightleftharpoons Cl_2 + H_2O.$$

Hypochlorites may be prepared by the action of chlorine on caustic alkalies when *kept quite cool*—

$$2\,NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

The most important derivative of this acid is bleaching powder, obtained by passing chlorine over dry slaked lime (see *Inorganic Chemistry, Mainly Metals*). Mineral acids or even carbon dioxide act on hypochlorites and liberate chlorine, and it is for use in this way that bleaching powder is produced on a large scale.

208. Chlorous Acid, $HClO_2$.—This acid has recently been isolated by the action of sulphuric acid on a solution of barium chlorite—

$$Ba(ClO_2)_2 + H_2SO_4 = BaSO_4 + 2\,HClO_2,$$

the barium sulphate being separated by filtration.

Chlorous acid is a colourless liquid which decomposes at ordinary temperatures into hypochlorous and chloric acids—

$$2\,HClO_2 = HClO + HClO_3.$$

The *chlorites* of several metals have been obtained. They are soluble in water and unstable. Sodium chlorite, $NaClO_2$, may be prepared by the interaction of sodium peroxide and chlorine dioxide—

$$Na_2O_2 + 2\,ClO_2 = 2\,NaClO_2 + O_2.$$

209. Chloric Acid, $HClO_3$.—This acid is obtained by adding dilute sulphuric acid to a solution of barium chlorate in just sufficient quantity to combine with the whole of the barium—

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2\ HClO_3.$$

The precipitate of barium sulphate is separated by decantation and the sodium solution evaporated in vacuo. By this means a liquid containing about 50 per cent. of acid can be obtained; any attempt at further concentration results in the decomposition of the acid into perchloric acid, oxygen, chlorine, and water—

$$3\ HClO_3 = HClO_4 + Cl_2 + O_2 + H_2O.$$

The concentrated solution is a colourless syrupy liquid possessing powerful oxidising properties; for example, a piece of paper moistened with it takes fire. Again, the acid possesses strong bleaching properties; thus sulphur dioxide is oxidised to sulphuric acid, and sulphuretted hydrogen to sulphur—

$$4\ SO_2 + 3\ H_2O + 2\ HClO_3 = 4\ H_2SO_4 + Cl_2O$$

$$4\ H_2S + 2\ HClO_3 = 4\ S + 5\ H_2O + Cl_2O.$$

The *chlorates* are all soluble in water. The alkali chlorates are prepared by the action of chlorine on *hot concentrated* solutions of caustic alkalies, the reaction taking the form—

$$6\ KOH + 3\ Cl_2 = \underset{\text{Potassium chlorate.}}{KClO_3} + 5\ KCl + 3\ H_2O.$$

The chlorate being much more insoluble, can be readily separated from the chloride by crystallisation.

Potassium chlorate is the most important of the chlorates; it finds extensive application in the arts. (*Inorganic Chemistry, Mainly Metals.*)

210. Perchloric Acid, $HClO_4$.—This acid is prepared by distilling potassium perchlorate with concentrated sulphuric acid under reduced pressure—

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4.$$

The distillate contains some water, but on redistilling with concentrated sulphuric acid the pure substance passes over as

a colourless, heavy, oily liquid which fumes in the air and is hygroscopic. It dissolves in water with evolution of heat, to form a series of hydrates containing from one to five molecules of water of hydration. Perchloric acid is the most stable of the oxyacids of chlorine, but it is nevertheless a very powerful oxidising agent, owing to its tendency to part with oxygen.

Thus it detonates violently when brought into contact with dry charcoal, and organic substances in general bring about its decomposition, many of them, *e.g.* paper, being inflamed. The acid does not, however, possess any bleaching properties, differing in this respect from the other oxyacids of chlorine. Perchloric acid is a strong acid, rapidly dissolving such metals as zinc with evolution of hydrogen and formation of the corresponding perchlorate—

$$Zn + 2\,HClO_4 = Zn(ClO_4)_2 + H_2.$$

The *perchlorates* are soluble in water, the least soluble being those of potassium and barium ; they are more stable than the chlorates, from which they may be distinguished by yielding no euchlorine when warmed with hydrochloric acid.

When potassium chlorate is fused and further heated till the mass becomes pasty, potassium perchlorate is formed, the change which has taken place being—

$$4\,KClO_3 = 3\,KClO_4 + KCl.$$

The perchlorate, being more insoluble than the chloride, may be obtained by dissolving the mass in water and allowing the perchlorate to crystallise out.

Oxyacids of Bromine.

211. Hypobromous Acid, HBrO, and Bromic Acid, $HBrO_3$.—No oxide of bromine is known, but two oxyacids, *hypobromous acid*, HBrO, and *bromic acid*, $HBrO_3$, have been prepared.

Hypobromous Acid, HBrO.—The methods of preparation and properties of this acid and its salts are so similar to those given for hypochlorous acid and its salts that a repetition of them is unnecessary.

Bromic Acid, $HBrO_3$.—An aqueous solution of this acid may be prepared from potassium bromate by a method similar to that used in preparing chloric acid.

Another method is to prepare the sparingly soluble silver bromate by adding silver nitrate to a hot solution of potassium bromate, when silver bromate is precipitated. This is filtered off and suspended in water, and bromine is added, when the following reaction takes place—

$$5\ AgBrO_3 + 3\ Br_2 + 3\ H_2O = 5\ AgBr + 6\ HBrO_3.$$

The silver bromide is removed by filtration and an aqueous solution of bromic acid remains.

Still another method of preparation is to pass chlorine into bromine water—

$$Br_2 + 5\ Cl_2 + 6\ H_2O = 2\ HBrO_3 + 10\ HCl.$$

Bromic acid closely resembles chloric acid in its properties. It is reduced by sulphur dioxide, by sulphuretted hydrogen, and by hydrogen bromide.

$$5\ HBr + HBrO_3 = 3\ Br_2 + 3\ H_2O$$

$$5\ SO_2 + 5\ H_2O + 2\ HBrO_3 = Br_2 + H_2O + 5\ H_2SO_4$$

$$3\ H_2S + HBrO_3 = 3\ H_2O + 3\ S + HBr.$$

Bromates.—When bromine is added to hot caustic potash a reaction takes place which is strictly analogous to that between chlorine and potash under similar conditions, a mixture of potassium bromide and bromate being formed—

$$6\ KOH + 3\ Br_2 = 5\ KBr + KBrO_3 + 3\ H_2O.$$

The bromate is much the less soluble salt of the two, and can be separated by fractional crystallisation.

The bromates are mostly easily soluble salts closely resembling the chlorates.

Oxides and Oxyacids of Iodine.

212. Introductory.—Iodine forms two oxides, iodine dioxide, IO_2, and iodine pentoxide, I_2O_5; and four oxyacids, viz. hypoiodous acid, HIO, iodic acid, HIO_3 ($I_2O_5 + H_2O = 2\ HIO_3$), meta-periodic acid, HIO_4, para-periodic acid, H_5IO_6.

213. Iodine Dioxide, IO_2 or I_2O_4.—This may be prepared by the action of concentrated nitric acid on dry powdered iodine *in the cold*. It is a yellow crystalline compound, and decomposes on heating into iodine and iodine pentoxide. On boiling with water it gives iodine and iodic acid—

$$10\,IO_2 + 4\,H_2O \rightleftharpoons 8\,HIO_3 + I_2.$$

214. Iodine Pentoxide, I_2O_5.—This is a white crystalline powder obtained by heating iodic acid to 180° C.—

$$2\,HIO_3 = I_2O_5 + H_2O.$$

It dissolves readily in water with evolution of heat, reforming iodic acid. At 300° C. it is decomposed into iodine and oxygen. It is a strong oxidising agent, and converts sulphur dioxide into sulphur trioxide—

$$5\,SO_2 + I_2O_5 = 5\,SO_3 + I_2,$$

and carbon monoxide into carbon dioxide at ordinary temperatures—

$$5\,CO + I_2O_5 = 5\,CO_2 + I_2.$$

215. Hypoiodous Acid, HIO.—An aqueous solution of hypoiodous acid may be prepared by a method analogous to that used for hypobromous acid, viz. the action of mercuric oxide on iodine suspended in water—

$$2\,I_2 + HgO + H_2O = HgI_2 + 2\,HIO.$$

It is similar in properties to hypobromous and hypochlorous acids, but much less stable.

216. Iodic Acid, HIO_3.—Nitric acid has no action on chlorine or bromine, but when heated with iodine, iodic acid is formed—

$$3\,I_2 + 10\,HNO_3 = 6\,HIO_3 + 2\,H_2O + 10\,NO.$$

This is the best method of preparing the acid.

Exp. 64. Introduce 5 grm. of iodine into a long-necked flask together with 50 grm. of strong nitric acid, and heat gently. The iodine will gradually disappear and copious brown fumes of nitrogen peroxide will be evolved (perform the experiment in a fume cupboard). When the action moderates heat more strongly, and continue heating till the

solution is colourless. Transfer the liquid to a porcelain dish and evaporate on the water-bath to small bulk. On cooling, crystals of iodic acid will separate out.

Iodic acid is also produced when chlorine is passed through water in which iodine is suspended—

$$5\ Cl_2 + 6\ H_2O + I_2 = 2\ HIO_3 + 10\ HCl.$$

Another method, resembling that used for chloric and bromic acids, consists in decomposing barium iodate with the calculated quantity of dilute sulphuric acid, decanting off the supernatant liquid from the precipitated barium sulphate and evaporating till crystals of iodic acid separate on cooling.

217. Properties of Iodic Acid.—Iodic acid is a colourless crystalline solid very soluble in water. It is a strong oxidising agent; thus, with sulphur dioxide and sulphuretted hydrogen respectively, it reacts as follows :—

$$2\ HIO_3 + 5\ SO_2 + 4\ H_2O = I_2 + 5\ H_2SO_4.$$

$$4\ HIO_3 + 10\ H_2S = 2\ I_2 + 5\ S_2 + 12\ H_2O.$$

Iodic acid and hydriodic acid at once undergo mutual decomposition, both losing their iodine—

$$HIO_3 + 5\ HI = 3\ I_2 + 3\ H_2O.$$

The liberation of iodine from iodic acid by the alkaloid morphine affords a convenient test for both substances, the free iodine being detected by its action on starch. Iodic acid possesses bleaching properties; thus it acts on litmus, first turning it red on account of its acid properties and then bleaching it.

218. Iodates.—By the action of caustic alkalies on iodine, iodates are formed, the reaction taking place either in hot or cold solution—

$$6\ KOH + 3\ I_2 = KIO_3 + 5\ KI + 3\ H_2O.$$

Another method of preparing potassium iodate consists in heating potassium chlorate with iodine—

$$2\ KClO_3 + I_2 = 2\ KIO_3 + Cl_2.$$

Iodine acts on free chloric acid in a similar manner, liberating chlorine and forming iodic acid. Now it will be remembered that *chlorine* was able to displace *iodine* from hydriodic acid and from potassium iodide, whereas here we have cases of *iodine* replacing *chlorine*; also hydrochloric is more stable than hydriodic acid, whereas iodic acid is more stable than chloric acid. There is, therefore, in both cases a *tendency for the formation of the more stable acid and its salts.*

The normal iodates of the alkali metals exhibit a great tendency to combine with iodic acid with formation of acid salts. Thus KIO_3 forms two such salts—

$KIO_3 \cdot HIO_3$ Potassium di-iodate.

$KIO_3 \cdot 2\,HIO_3$ Potassium tri-iodate.

The majority of the iodates are insoluble or only slightly soluble in water, those of the alkali metals being the most soluble.

On heating, most iodates lose oxygen and iodine, and finally leave a residue of the oxide of the metal (though a periodate may be formed as an intermediate product); but those of the alkali metals lose oxygen only, leaving the iodide of the metal—

$$2\,Zn(IO_3)_2 = 2\,ZnO + 2\,I_2 + 5\,O_2.$$

$$2\,KIO_3 = 2\,KI + 3\,O_2.$$

219. Periodic Acid.—There are probably several periodic acids, the two most important are H_5IO_6, *para*-periodic acid, and HIO_4 *meta*-periodic acid.

Para-periodic acid is prepared by the action of water on its acid silver salt, $Ag_2H_3IO_6$, the following change taking place—

$$5\,Ag_2H_3IO_6 = 2\,Ag_5IO_6 + 3\,H_5IO_6.$$

It may also be obtained by the action of iodine on perchloric acid—

$$4\,H_2O + 2\,HClO_4 + I_2 = 2\,H_5IO_6 + Cl_2,$$

or by the action of sulphuric acid on barium para-periodate—

$$Ba_3(IO_6)_2 + 5\,H_2SO_4 = 5\,BaSO_4 + 2\,H_5IO_6.$$

The barium sulphate is removed by filtration and the para-periodic obtained by evaporation.

Para-periodic acid is a colourless crystalline solid readily soluble in water. It possesses strong oxidising properties.

On heating para-periodic acid to 100° C. at low pressure HIO_4, *meta-periodic acid* is said to be obtained.

Periodates of the alkalies may be prepared by the action of chlorine on the iodate; other periodates by double decomposition of these with soluble salts of the metals. Barium para-periodate is a body of great stability, and may be obtained by heating barium iodate to redness—

$$5\ Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4\ I_2 + 9\ O_2.$$

Most periodates are insoluble or sparingly soluble in water.

The para-periodates are derived from the acid H_5IO_6; the meta-periodates are derived from HIO_4, others from H_3IO_5, and others again from more complex acids. All of them can, however, be considered as being derived from acids obtained by combining one or more molecules of water with the oxide I_2O_7, which has not yet been prepared. Thus—

$$I_2O_7 + H_2O = H_2I_2O_8 = 2\ HIO_4.$$
$$I_2O_7 + 2\ H_2O = H_4I_2O_9.$$
$$I_2O_7 + 3\ H_2O = H_6I_2O_{10} = 2\ H_3IO_5.$$
$$I_2O_7 + 5\ H_2O = H_{10}I_2O_{12} = 2\ H_5IO_6.$$

QUESTIONS.—CHAPTER XVI.

1. What is the action of dry and of moist chlorine on mercuric oxide?

2. Describe the preparation and chief properties of chlorine peroxide.

3. What bodies may be obtained by acting on a solution of caustic potash with chlorine? Give equations.

4. Compare and contrast the chlorates and iodates.

5. Give the preparation of chloric and perchloric acids and compare the properties of these bodies.

6. Give the preparation and properties of bromic acid and the bromates.

7. How is iodic acid prepared? What is its action on (1) sulphurous acid, (2) hydriodic acid, (3) sulphuretted hydrogen?

8. Write a short account of the *iodates*.

9. State what you know of the periodic acids and the periodates.

CHAPTER XVII.

NITROGEN. THE ATMOSPHERE. HYDRIDES OF NITROGEN.

Nitrogen, N_2.

220. Introductory.—Nitrogen is the first member of a group of elements, nitrogen, phosphorus, arsenic, antimony, and bismuth, which either in themselves or their compounds exhibit considerable analogy to one another. The first two members only are usually classed with the non-metals.

The elements forming this group show a transition in physical properties as the atomic weight increases, nitrogen being gaseous at the ordinary temperature, whilst phosphorus is solid but easily vaporised, the other members being more difficult to volatilise.

Speaking more particularly with regard to nitrogen and phosphorus, it will be seen by a reference to the following pages that they resemble one another :—

(1) In forming hydrides of similar composition NH_3, PH_3, both of which combine directly with haloid acids yielding the ammonium and phosphonium salts.

(2) In forming a characteristic series of oxides, some of which yield powerful acids.

221. Occurrence.—Nitrogen occurs mixed with oxygen in the atmosphere, of which it forms nearly four-fifths the volume.

Although it does not enter to any large extent into the composition of animal and vegetable tissues, it is, notwithstanding, a very constant and essential constituent of such tissues. The nitrogen of plants is obtained chiefly through

the medium of the soil, in which small quantities of nitric acid, nitrates, and ammonium salts always occur. Animals cannot assimilate nitrogen directly, and derive their supply from the plants.

222. Preparation.—Nitrogen can be obtained from air by any process which removes oxygen. A convenient method of bringing this about in practice is to pass air over heated copper contained in a hard glass tube. The nitrogen so obtained is not pure, for air contains a number of other inert gases, chiefly argon, in addition to nitrogen (see § 226). However, nitrogen is obtained commercially from air by the fractional distillation of liquid air (see § 239). A convenient laboratory method of preparing pure nitrogen is to heat a solution of ammonium nitrite—

$$NH_4NO_2 = N_2 + 2\,H_2O.$$

In practice a mixture of ammonium chloride, NH_4Cl, and sodium nitrite, $NaNO_2$, is used instead of ammonium nitrite, since both NH_4Cl and $NaNO_2$ are common salts, whereas NH_4NO_2 is an unstable compound. We may suppose that the NH_4Cl and $NaNO_2$ undergo double decomposition with formation of NH_4NO_2 and NaCl, and that the ammonium nitrite is then decomposed according to the equation given above.

Exp. 65. Introduce about 15 grm. of sodium nitrate and 10 grm. of ammonium chloride into a small flask, and add about 100 c.cm. of water. Fit the flask with a cork carrying a delivery tube. Warm gently and collect the nitrogen over water at the pneumatic trough.

If the nitrogen is required dry, it should be passed through a sulphuric acid wash-bottle and collected over mercury.

Another method of preparation is to heat ammonium bichromate $(NH_4)_2Cr_2O_7$.

$$(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3 + 4\,H_2O.$$

Instead of ammonium dichromate, it is more convenient to use a mixture of ammonium chloride and potassium dichromate, which serves the same purpose. Nitrogen can also be obtained by the action of chlorine on a concentrated

solution of ammonia, taking care to keep a large excess of ammonia present throughout the experiment, thus preventing the formation of the explosive chloride of nitrogen—

$$8\ NH_3 + 3\ Cl_2 = N_2 + 6\ NH_4Cl.$$

This reaction may be represented in two stages—

$$2\ NH_3 + 3\ Cl_2 = N_2 + 6\ HCl.$$
$$6\ NH_3 + 6\ HCl = 6\ NH_4Cl.$$

223. Properties of Nitrogen.—Nitrogen is a colourless, odourless gas, which does not support life or combustion. Nitrogen does not combine with oxygen under ordinary conditions; but it may be made to do so by means of an electric arc, when nitrogen peroxide is formed. It is somewhat lighter than air, and condenses to the liquid form at — 196° C. and freezes at — 210·5° C.; it is slightly soluble in water, less so than oxygen (see § 36).

The chief characteristic of nitrogen is its inertness, but at the same time there are some elements with which it readily combines directly to form nitrides, *e.g.* magnesium, boron, titanium, and tungsten; the last two do not require heating if they are in a finely-divided state. Nitrogen also combines directly with barium, strontium, lithium, aluminium, silicon, and carbon. Hydrogen unites with nitrogen when the mixture under pressure is passed over heated iron at 500°. This is the basis of the *Haber Process* for the manufacture of ammonia.

Calcium carbide combines with nitrogen to form calcium cyanamide—

$$CaC_2 + N_2 = CaCN_2 + C.$$

Under these conditions barium carbide gives barium cyanide.

$$BaC_2 + N_2 = Ba(CN)_2.$$

224. Active Nitrogen.—In 1911 Strutt discovered that when an electric discharge is passed through nitrogen under reduced pressure, an active form of the gas is obtained. This "active" nitrogen converted mercury, cadmium, zinc, etc.,

into the corresponding nitrides; and with acetylene and chloroform gave cyanogen—

$$C_2H_2 + 2\,N = (CN)_2 + H_2,$$

but it did not react with hydrogen. It has been suggested that this active form of nitrogen is monatomic, but the problem is not yet solved.

The Atmosphere.

225. The Atmosphere. History.—Before the time of Boyle (ca. 1650), air was believed to be a simple substance. Boyle's pupils, Hooke and Mayow, showed by experiment that the atmosphere was composed of at least *two gases*. However, this fact was not used for nearly one hundred years, during which time the Phlogiston Theory flourished. In 1755 Black recognised the presence of carbon dioxide in air. Quantitative experiments on the atmosphere were conducted chiefly by Lavoisier, Scheele, and Priestley about 1770, and oxygen was discovered as the " active " part of air by Priestley and Scheele, independently, in 1774. Both Priestley and Cavendish showed that there was a constituent in the atmosphere which gave saltpetre when sparked with oxygen over potash. This constituent was named nitrogen by Chaptal in 1792 (from the Greek, to become nitre).

Cavendish, in 1784, had shown that when air was sparked with excess of oxygen over potash a small quantity, about $\frac{1}{120}$ of the whole remained; but it was not until over 100 years later that this phenomenon was explained after Lord Rayleigh's discovery of argon and the inert gases (see § 227).

226. Composition of the Atmosphere.—The atmosphere is chiefly composed of nitrogen and oxygen. With these are associated argon and the other inert gases, carbon dioxide, ammonia, water vapour, and other gases, the amounts of which vary according to the circumstances. From whatever locality the air has been obtained, the relative proportions of nitrogen and oxygen exhibit only slight variations. The following table gives the average composition of the atmosphere :—

Constituent.	% by Volume.	% by Weight.
Nitrogen	78·03	75·51
Oxygen	20·99	23·15
Inert Gases	0·95	1·30
Carbon dioxide	0·03	·04
Water Vapour	varying	varying
Impurities	varying	varying

The discovery of the inert gases forms a very interesting chapter in the history of chemistry.

227. The Inert Gases of the Atmosphere.—In the year 1894 Lord Rayleigh noticed that the density of nitrogen obtained from the air was about 0·4 per cent. greater than that of nitrogen prepared by chemical methods. He then repeated Cavendish's experiment and found that his results were correct. The gas left after sparking was examined by the spectroscope and it was found that it was *not* nitrogen. The only explanation which could be offered was that air contained a small quantity of another inert gas in addition to nitrogen.

Ramsay took up the question and succeeded in isolating this gas; he passed air freed from carbon dioxide and water vapour over red-hot copper which removed the oxygen, and then over red-hot magnesium which removed the nitrogen. The residue amounted to about 1 per cent. of the air used, and consisted of a very inert gas which Ramsay could not decompose or cause to combine with any known substance. He came to the conclusion that the new gas was an *element*, and on account of its inertness he called it *argon* (Greek, *argos*, inert or idle).

Argon forms no chemical compounds, and since it has no equivalent weight its molecular weight has been determined from its vapour density (19·94); hence the molecular weight is 39·88. The molecule of argon has been shown to contain one atom, the atomic weight is therefore 39·88. Argon liquefies at — 187° C. and solidifies at — 189·5° C. Argon is used commercially for filling gas-filled electric lamps. It can be obtained from liquid air in fairly large quantities.

Later Ramsay discovered several other new elementary gases in the atmosphere, namely *helium* (Greek, *helios*, the sun), *neon* (Greek, *neos*, new), *krypton* (Greek, *kryptos*, hidden), and *xenon* (Greek, *xenos*, stranger). He fractionally distilled large quantities of liquid air, and from the lowest boiling portions isolated two elements, helium and neon. From the portions boiling at a higher temperature than oxygen, nitrogen, and argon, he isolated krypton and xenon. These elements are only present in exceedingly small quantities in the atmosphere; they are all very inert like argon and have not, up to the present, been induced to combine with any known substance. As in the case of argon, so with these other elements the molecule contains one atom.

Helium has been found in some uranium ores and in certain springs as well as in the atmosphere. It is the last gas which has been made to undergo liquefaction and it has the lowest boiling point of any known substance, — 269° C.

The atomic weights of neon, krypton, xenon, and helium are respectively 20, 81·75, 128 and 4.

228. Determination of the Composition of the Atmosphere by Volume.—The most accurate method is to remove oxygen from an enclosed volume of air, the pressure and temperature of which are known, by heating a spiral of copper wire in it by means of an electric current. On reducing the temperature to the original value and measuring the pressure of the residual gas the percentage of oxygen present can be calculated.

The experiment is carried out in Jolly's apparatus shown in Fig. 41. A is a glass globe of about 100 c.cm. capacity, provided with an exit-tube E, at the end of which is a three-way tap D. This tap is connected with (1) a short tube F, open at the end, and (2) a pressure-gauge consisting of two glass tubes, B and C (of which C is open to the atmosphere), connected by rubber tubing and containing mercury. The tube C can be raised and lowered, and behind it is placed a scale so that the level of the mercury can be read off. By suitably turning the tap D it can be arranged that A is connected with either F only or B only, or with both F and B, or that it is shut off from both.

The first part of the operation consists in filling the globe with dry air; this is done by turning the tap D so that A is connected with the tube F, and exhausting the globe by means of a pump connected to F.

Air, which has been dried by concentrated sulphuric acid, is now introduced through F. The globe is next surrounded by a vessel containing melting ice to reduce the temperature of the gas to 0° C.; when this has been accomplished the tube C is raised till the mercury in B just reaches to the top of the tube, *i.e.* the point *x*, the tap being so turned that A is connected with B only. The height of the mercury in C is then read and also the barometer. The pressure of the air in A is calculated by combining the difference in mercury levels in B and C with the barometric pressure. (If the level of C is *higher* than the point *x* the difference must be *added* to the barometric pressure, if *lower* it must be subtracted from that pressure.

The vessel containing the melting ice is now removed, A being shut off from both B and F, and the copper spiral, G, is heated by passing a current of electricity through it, when the oxygen present is converted into cupric oxide. A is now surrounded again by melting ice, and its temperature once more reduced to 0° C. C is lowered considerably (to prevent mercury being sucked into the horizontal tube on opening the tap), and A and B are then put into connection. C is adjusted till the level of mercury in B just reaches *x*, the level in C is read and the pressure of the residual gas calculated as before.

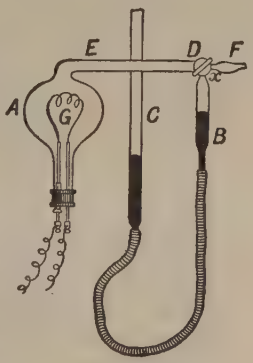


Fig. 41.

Let the initial pressure be P and the final pressure P′. Then the reduction of pressure due to removal of oxygen is P − P′. Consequently, since the temperature was the same (0° C.) in both cases, the percentage of oxygen is $\frac{P - P'}{P} \times 100$.

229. Determination of the Composition of the Atmosphere by Weight.—A method due to Dumas consists in passing the air over red-hot copper, with which the oxygen combines, as in the experiment just described.

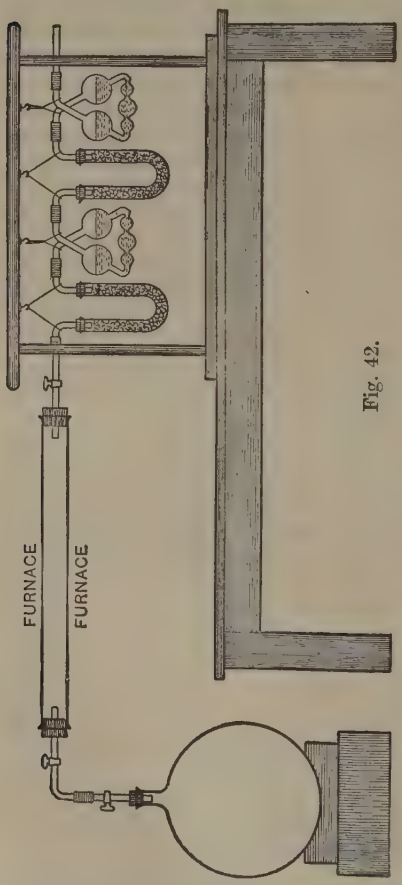


Fig. 42.

The air is previously freed from carbon dioxide and moisture by being passed over potash and concentrated sulphuric acid. The apparatus used is shown in Fig. 42; it consists essentially of a large glass globe, to which is attached a tube containing metallic copper, and heated in a furnace. The globe is first rendered vacuous by means of a good air-pump, the stopcock is closed, and the globe carefully weighed. The tube containing the copper is then rendered vacuous, closed, and weighed.

The copper having been heated to redness, the stopcock is opened sufficiently to allow a slow current of purified air to pass through the tube and into the glass globe. On the way, it is deprived of its oxygen, and if the experiment has been carefully conducted, only nitrogen and argon pass into the globe.

After the apparatus has quite cooled, the globe is again weighed, and the increment gives *the weight of the nitrogen and argon.* The tube is also weighed again, and the increase there shows *the weight of the oxygen*, together with a little nitrogen and argon which remain in the tube. After exhausting and weighing again, the decrease in weight is added to the increase in weight of the globe to obtain the total nitrogen and argon. The oxygen is given by the difference of the two weighings of the *exhausted* tube.

A series of such determinations gave the composition by weight of air as—

Nitrogen and the inert gases	76·995
Oxygen	23·005.

The proportions of the inert gas have been determined as follows:—The total volume of the inert gases was first found by passing atmospheric nitrogen over heated magnesium. The amount of argon was obtained by subtracting the quantities of helium, krypton, neon, xenon, found by other methods. The proportions of the others were found by fractionally distilling liquid air.

230. Water Vapour in Air.—The amount of water vapour varies with the temperature and the degree of saturation of the air, for the higher the temperature of the air, the more moisture will it take up before it is saturated. The average amount is somewhat under 1 per cent. by volume, but in warm, moist climates may approach 4 per cent. It may be measured by observations on the dewpoint (see textbooks on physics), or by passing a known volume of air over calcium chloride contained in U-tubes, and noting the increase in weight of the tubes.

The amount of water vapour which the air can contain may be estimated by the fact that 1 cub. ml. of air saturated at 35° would deposit, if cooled to 0°, 140,000 tons of rain. But while the air is seldom completely saturated, it never contains less than $\frac{1}{10}$ of the possible amount.

231. Carbon Dioxide in Air.—The amount of this gas in air varies considerably, according to the locality from which the sample of air is taken. In country air there are from three to four volumes of CO_2 in 10,000, but in towns the amount is larger, and may reach seven or eight volumes. In badly-ventilated dwellings even ten-fold the normal amount of carbon dioxide may occur. The determination of carbon dioxide is a matter of importance, especially in the case of indoor air, since it serves to show the efficiency of ventilation.

The presence of carbon dioxide in air may be shown by exposing lime-water in a shallow dish; the lime-water is soon covered with a thin pellicle, owing to the formation of calcium carbonate or chalk, which is insoluble in water—

$$\underset{\text{Calcium hydroxide.}}{Ca(OH)_2} + CO_2 = \underset{\text{Calcium carbonate.}}{CaCO_3} + H_2O.$$

Baryta water may, by Pettenkofer's method, be used as a means of determining the amount of carbon dioxide in air. A known volume of a solution of baryta (which is alkaline) of known strength is shaken up with a measured quantity of air, say 10 litres; part of the baryta is converted into barium carbonate (a neutral body), whilst part remains unaltered. The amount of alkali (the baryta) is now smaller by reason of the conversion of part of it into carbonate by the carbon dioxide. The more carbon dioxide is present, the greater will be the amount of baryta converted into barium carbonate, and the greater will be the difference between the amount of alkali originally taken and that remaining afterwards. By ascertaining the amount of oxalic acid required to neutralise a known volume of the original baryta water, and that required to neutralise the liquid which remains after partial neutralisation, as already described, the quantity of carbon dioxide in the 10 litres of air may be ascertained.

232. Other Impurities in Air.—The remaining impurities, such as suspended dust and carbon, ammonia, sulphur compounds, hydrochloric acid, and chlorides, occur in much smaller and more variable quantities. During thunderstorms oxides of nitrogen are formed, and these give rise to nitrous and nitric acid; ozone is also probably produced under such

circumstances. The ammonia, carbon (soot), and sulphur compounds occur in larger quantity in the vicinity of towns, from the combustion of coal, or where decaying refuse is found.

The hydrochloric acid and chlorides come for the most part from manufacturing operations, though it is significant that, especially during high wind, the air in the neighbourhood of the sea contains much more sodium chloride than is usual.

233. The Relation of Animal and Plant Life to Air.—By breathing on a cool glass surface, and by expelling air from the lungs through lime-water, it is easy to demonstrate that expired air contains large quantities of moisture and carbon dioxide. Indeed the expired air from man contains usually over 4 per cent. of carbon dioxide, that is, over one hundred times as much as normal air.

(*a*) *The agencies at work in producing carbon dioxide are*—(1) Respiration of animals and plants; (2) combustion of fuel; (3) decay of organic matter; (4) subterranean causes.

Faraday calculated that nearly five million tons of carbon dioxide were contributed daily to the atmosphere by these processes. Under such a contribution the air would slowly get more and more charged with carbon dioxide, and the percentage of oxygen would diminish.

(*b*) *There are, however, processes constantly in operation which act in the opposite direction, viz.*—

(1) In the process of assimilation in plants, the green colouring matter (chlorophyll), in presence of direct or diffused sunlight, effects the decomposition of carbon dioxide and liberates oxygen.

(2) Carbon dioxide being moderately soluble in water is carried down by rain, and is also taken up by surface waters and sea water.

The precise extent to which the loss and gain counteract one another is difficult to estimate, but that plant life is an important factor is shown by actual observations on the living plant, and by the variations in the amount of carbon dioxide in air in the neighbourhood of forests in the daytime,

when the foliage is exposed to the sun's rays, as compared with night, when assimilation is checked and only respiration goes on.

234. Is Air a Compound or a Mixture of Nitrogen and Oxygen?—We have seen that a chemical compound shows the following characters :—

(1) It possesses a *definite* composition (§ 18).

(2) The weights of the elements composing it are in proportion to the atomic weights, or in some simple multiple proportion of the atomic weights. This follows from the Atomic Theory (see Chap. III.).

(3) The compound shows distinctive physical and chemical properties, the individual properties of the constituent elements being more or less completely concealed (§ 14).

(4) When combination takes place, heat is usually evolved.

(5) When gases combine to form a gaseous compound there is generally a contraction in volume, thus—

2 vol. of hydrogen + 1 vol. of oxygen form 2 vol. of water vapour.

3 vol. of hydrogen + 1 vol. of nitrogen form 2 vol. of ammonia.

(6) The simple solution of a gas in water does not affect its chemical composition ; for instance, if we dissolve ammonia or carbon dioxide in water, and then, by boiling the solution, expel the gas again, it will be found to be unaltered in character or composition.

Now let us apply these tests to air.

(1) The composition of air varies very little under different circumstances, but even such small variations as are found in its composition do not occur in the case of chemical compounds.

(2) If we divide the relative proportions by weight of nitrogen and oxygen in the air by the atomic weights of nitrogen and oxygen, we shall see whether any simple multiple relation is shown. Of the 76·995 per cent. of nitrogen and

argon present in air 0·937 per cent. is argon, so that the percentage of nitrogen is 76·995 — 0·937 = 76·058. We have therefore—

$$\text{Nitrogen } \frac{76{\cdot}058}{14} = 5{\cdot}433\,; \quad \text{Oxygen } \frac{23{\cdot}005}{15{\cdot}96} = 1{\cdot}441\,;$$

$$\text{And } 5{\cdot}433 : 1{\cdot}441 :: 3{\cdot}77 : 1.$$

That is, to be even approximately in agreement with the results of analysis we should have to assume a compound $N_1 O_4$ (3·77 : 1 = 15·08 : 4). The same result may be arrived at by considering the volume relations of nitrogen and oxygen in air.

(3), (4), and (5) Nitrogen and oxygen retain their characters with slight modification in air, and a mixture of the two gases in the proper proportions shows precisely the same characters in all respects as air. No heat is evolved when they are brought together, nor does any contraction in volume take place.

(6) We have seen (§ 39) that when air is shaken up with water, a greater proportion of oxygen dissolves than nitrogen, owing to the greater degree of solubility of oxygen, so that whilst in the air originally taken, one volume of oxygen is associated with approximately four volumes of nitrogen, air dissolved in water consists of one volume of oxygen associated with two volumes of nitrogen.

On all these grounds, therefore, we must admit that air is simply a *mixture* of nitrogen and oxygen. The following additional reasons may be mentioned :—

(7) The constituents of air can be partly separated by diffusion, for, owing to the difference in density of nitrogen and oxygen, they do not diffuse through a porous membrane at equal rates (see § 33); if the gases were combined the compound would diffuse *as a whole.*

(8) When liquid air boils the nitrogen distils off before the oxygen and argon.

(9) The refractive index of air is the mean of those of oxygen and nitrogen; in the case of compounds the value

is invariably found to be either above or below the mean of the values for the constituents.

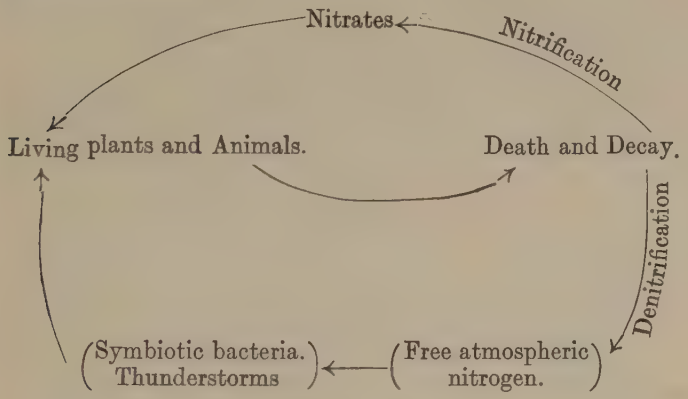
235. Fogs.—Fogs are caused by condensation of water vapour induced by dust. That dust is the cause of fog formation is proved by the fact that in filtered air fogs cannot form. Analysis of the deposit left after a fog showed it to consist of carbon, hydrocarbons, sulphuric acid, iron and its oxides, and silica. During a fog, too, the amount of carbon dioxide increases enormously and reaches from three to five times the normal amount.

236. The Nitrogen Cycle.—Nitrogen is a necessary constituent for all forms of life. Animals, and nearly all plants, cannot assimilate free nitrogen. Animals obtain their supply from the plants in the form of proteins, which are complex organic compounds containing nitrogen. The plants are able to get their supply of nitrogen from the nitrates or other nitrogenous compounds present in the soil, and to build up proteins by life processes. A few plants, notably Leguminosae (peas, beans, etc.), are able to fix free nitrogen by means of bacteria which are called symbiotic, and which live in numerous small nodules on their roots.

The soil would thus become gradually drained of its nitrogen by plants if there were not some agencies at work to replenish the supply. Decaying organic matter of all kinds, manure, dead plants, animal excreta, and urine, return nitrogen to the soil, but in such a form that the plants cannot utilise it. The nitrogenous organic matter is however attacked by bacteria which cause it to decay, and then convert it successively into ammonia, then into nitrites, and finally into nitrates; this process is called *nitrification*. Some of the nitrates thus produced are acted upon by a certain class of bacteria to produce nitrogen, a process which is called *denitrification*. A certain amount of nitrogen is also returned to the soil in the form of nitric acid, and ammonium nitrate which are produced during thunderstorms.

The amount of nitrogen taken from the soil is, however, greater than the quantity returned in the ways described,

and therefore much nitrogen is now added to the soil in the form of artificial manures which contain nitrates or ammonium salts. These processes can be conveniently shown by the following scheme :—



237. Liquid Air. Preparation.—Air is now liquefied in large quantities by two general methods.

(1) The Linde and Hampson processes in which use is made of the fact that when a gas at high pressure is allowed to expand through an orifice, part of the heat energy of the gas is used up in overcoming the attraction of the molecules for each other and moving them further apart. There is consequently a fall in temperature.

(2) The Claude process in which use is made of the cooling effect produced by a compressed gas expanding against an external resistance.

The Linde and Hampson Processes.—In all processes for the liquefaction of air it is essential that the air used is purified and dried. Further, in each of the two general methods mentioned above liquefaction depends on an arrangement for regenerative cooling, *i.e.* the compressed air that enters the plant is previously cooled by the expanded air coming from the plant, and in this way the cooling effects of the gas

are accumulated in the gas. Briefly the method is as follows :—

Highly compressed air (freed from carbon dioxide and water vapour) is pumped down a spiral tube A (Fig. 43), and escapes through a small hole in the bottom B, the escape being regulated by the valve D. In so doing it expands and becomes cooler. The cold gas is then allowed to pass up *outside* the tube C, and is then again compressed and pumped back into the tube A. During its upward passage it cools the compressed gas passing down the tube. This cooled compressed gas then escapes and becomes still colder. The process is repeated, till finally the gas liquefies on expansion. The description will be understood after an examination of the diagram, Fig. 43. In the Linde Process the purified air is compressed to 200 atmospheres, previously cooled to — 35° by means of liquid ammonia, and allowed to expand to a pressure of 50 atmospheres.

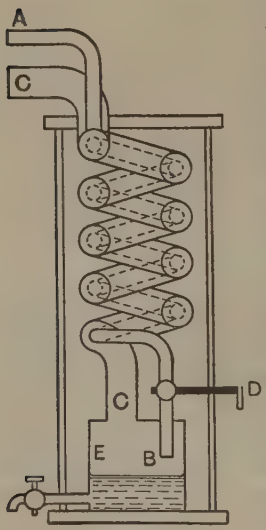


Fig. 43.

Claude's Process.—After a great deal of difficulty Claude, in 1902, liquefied air by allowing compressed air at 40 atmospheres to expand in an ordinary compressed air motor, and in this way obtained extreme cooling effects. The compressed air is cooled owing to the external work done by the expanding gas.

Briefly, the air purified from carbon dioxide and water vapour and compressed to 40 atmospheres is cooled to — 140° (*i.e.* the boiling point of liquid air at 40 atmospheres) by expanding to a pressure of about 4 atmospheres in an engine which is so arranged that it is coupled up to assist the compresser. The liquid air formed is drawn off after being brought to atmospheric pressure, and the cold gases which escape are used to cool the compressed gas.

238. Properties of Liquid Air.—Liquid air is slightly blue, mobile liquid; its density is 1·0 approximately, and its boiling point between — 183° and — 196° according to its composition. Liquid air is a very important substance; commercially it has many uses; *e.g.* for the preparation of oxygen, nitrogen, and argon; as a cooling agent, and for the production of low temperatures; when mixed with charcoal as a blasting explosive; and for the production of enriched air for respiration. As its critical temperature is — 140°, it has to be kept in special containers, the principle of which was applied by Dewar. These containers are double walled bottles in which there is a vacuum between the two walls and the inner sides of which are coated with silver (see Fig. 44).

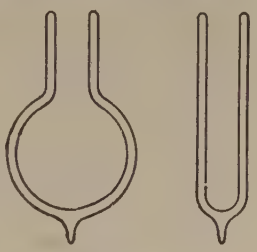


Fig. 44.

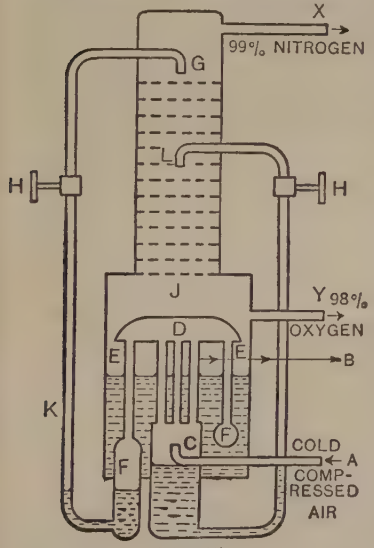


Fig. 45.

239. Separation of Oxygen and Nitrogen from Liquid Air.—In 1895 Linde was able to separate oxygen from liquid air by the *counter current principle*, a principle similar to that described for the preparation of liquid air. Linde's process, however, was improved on by Claude in 1903, whereby practically pure oxygen and nitrogen are now obtained. A diagrammatic representation of the apparatus is shown in Fig. 45. Briefly, cold compressed air enters at A at a pressure of 5 atmospheres, and rises

through pipes B which are surrounded with liquid oxygen. The air is partially liquefied, and the liquid is collected in C; the vapours pass on to D and descend again through concentric pipes E surrounded by liquid oxygen to F, where all the gas is liquefied. This liquid in F is very rich in nitrogen, and is forced by the pressure in B up K to G, the top of the rectifying column; similarly the liquid in C is forced to L.

The oxygen in C is at its boiling point at atmospheric pressure, while the liquid, rich in nitrogen at G, is suddenly placed under atmospheric pressure, and hence boils rapidly, losing practically all its nitrogen which passes out through X. The descending liquid gets warmer as it goes down the rectifying column, whilst ascending gases get steadily cooler. Thus practically all the oxygen becomes liquefied and all the nitrogen in the ascending stream is distilled off.

The result is to collect liquid oxygen in J, which can be evaporated by the latent heat of the incoming gases which condense in B and E, and to get nitrogen gas (0·2 — 1 per cent. oxygen) at X. The oxygen (2 — 4 per cent. nitrogen) escapes through Y. H H are values to regulate the flow and the pressure.

Compounds of Nitrogen with Hydrogen.

Ammonia	NH_3
Hydrazine	N_2H_4
Hydrazoic acid or azoimide	N_3H
Ammonium hydrazoate *or* Ammonium azide	$NH_3.N_3H$ or N_4H_4
Hydrazine hydrazoate *or* Hydrazine azide	$N_2H_4.N_3H$ or H_5N_5

Ammonia, NH_3.

240. History.—The salt, sal-ammoniac, has been known for many centuries, and was formerly prepared by heating camels' dung. It was probably first called *sal-armeniac*, as it was found native in Armenia. The name sal-ammoniac was

first given to a mixture of common salt and soda which was found near the temple of Jupiter Ammon in the Libyan desert, but was later changed to mean the salt obtained above. Aqueous solutions of ammonia were prepared from sal-ammoniac by the action of alkalies, and also by distilling such animal substances as hoofs and horns—whence the old name for ammonia, *spirits of hartshorn*. Priestley, in 1774, first isolated ammonia gas by collecting it over mercury instead of over water, and he called it "alkaline air"; later, Bergman, in 1782, called the gas ammonia. Berthellot, in 1785, showed that the gas is decomposed by electric sparks into nitrogen and hydrogen.

241. Occurrence.—Ammonia, or its compounds, exist in small quantities in air and in natural waters, being produced either from the nitrogen present in the air, or by the action of bacteria from refuse matters in the soil. It is found in large quantities as ammonium sulphate in the *Soffioni* in Tuscany.

242. Preparation.—In the laboratory ammonia is usually prepared by heating a mixture of ammonium chloride and slaked lime, $Ca(OH)_2$—

$$2\,NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\,NH_3 + 2\,H_2O.$$

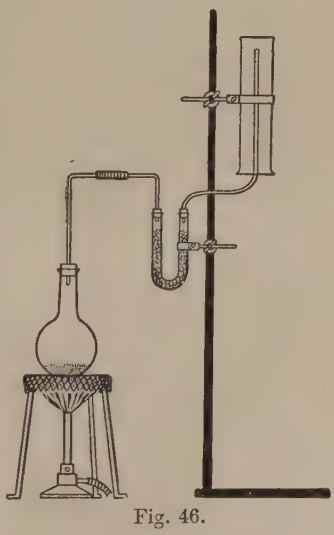


Fig. 46.

Exp. 66. Weigh out about 10 grm. of ammonium chloride and 20 grm. of dry slaked lime and grind them up in a mortar till they are in a state of a fine powder and intimately mixed. Introduce the mixture into a small dry round-bottomed flask, and connect this with a U-tube containing lumps of quicklime or caustic soda, as shown in Fig. 46. Now heat the flask gently when ammonia will be evolved, and after

being dried by the lime or caustic soda in the U-tube may be collected by upward displacement, being much lighter than air. Ammonia can also be collected over mercury, but not over water in which it is very soluble.

The ordinary drying agents for gases—sulphuric acid, calcium chloride, and phosphorus pentoxide—cannot be used in the case of ammonia, since it combines readily with them.

243. Industrial Preparation.—Ammonia and its compounds are used very extensively in commerce. The methods employed for the industrial preparation of ammonia can be grouped conveniently as follows :—

(1) From animal and vegetable products containing nitrogen.

(2) Synthetic methods using atmospheric nitrogen.

(3) Other methods.

(1) From Animal and Vegetable Products.—Whenever animal or vegetable products containing nitrogen are strongly heated in closed retorts (air being excluded) and especially when they are heated with lime or other alkalies, ammonia is given off.

In this way large quantities of ammonia are obtained during the distillation of coal (which contains about $1\frac{1}{2}$ per cent. of nitrogen), the coal gas being cooled and then washed, by which means any ammonia is separated and obtained in solution. The *gas-liquor* thus obtained is distilled after the addition of lime and the ammonia set free is passed into sulphuric acid and used as a fertiliser, etc., in the form of ammonium sulphate—

$$2\,NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

By the destructive distillation of bituminous shale, an ammoniacal distillate is obtained which can be treated as described above to form ammonium sulphate. This method is used extensively in Scotland.

(2) Synthetic Methods.—The synthetic method for the preparation of ammonia depends on the fact that under certain conditions nitrogen unites directly with hydrogen to form ammonia.

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3.$$

This reaction is exothermic and reversible. Also it will be observed that four volumes of the mixture of nitrogen and hydrogen produce two volumes of ammonia, and thus an increase of pressure should favour the formation of ammonia according to Le Chatelier's Law (see *Inorganic Chemistry, Mainly Metals.*) The following table shows the best conditions for working :—

PERCENTAGE OF AMMONIA IN THE EQUILIBRIUM MIXTURE.

Temperature.	1 Atmos.	50 Atmos.	100 Atmos.	200 Atmos.
200° C.	15	—	81	86
450° C.	0·24	9·5	16·2	25·3
500° C.	0·13	5·7	10·4	17·6
550° C.	0·08	3·7	6·9	12·0
600° C.	0·05	2·3	4·5	8·2
800° C.	0·012	—	1·15	2

The velocity of the reaction at low temperatures is, however, very slow, though at higher temperatures the amount of ammonia formed is considerably lowered. It has been found that the best conditions are a temperature of 550°, a pressure of 200 atmospheres, and the use of a catalyst, which, in the *Haber Process*, is a mixture of finely-divided iron and molydenum. To prevent the reverse reaction the ammonia so formed is cooled and dissolved in water, or liquefied. The nitrogen is obtained from liquid air and the hydrogen from water gas or by any other industrial method. The gases are carefully purified otherwise the catalyst is " poisoned " quickly.

(3) Other Methods. (*a*) *Cyanamide Process.*—In this process calcium cyanamide, $CaCN_2$ is hydrolysed by steam under pressure—

$$CaCN_2 + 3\,H_2O = CaCO_3 + 2\,NH_3.$$

Calcium cyanide is obtained cheaply, by passing nitrogen over calcium carbide heated in the electric furnace.

(*b*) *Serpek Process.*—This process depends on the fact that

aluminium nitride is decomposed by caustic soda to form ammonia and sodium aluminate.

$$AlN + 3\,NaOH = NH_3 + Na_3AlO_3.$$

244. Properties.—Ammonia is a colourless gas, having a very pungent but not disagreeable odour if diluted with much air; in the pure condition it is injurious when breathed in quantity. At — 33° C. under ordinary pressure, and at 0° C. under a pressure of 7 atmospheres, dry ammonia condenses to the liquid form (see Fig. 47, Carré's apparatus). Ammonia freezes to a solid, melting at — 78° C.

Exp. 67. Fill a litre flask by displacement with dry ammonia, and show its solubility in the same way as already described in the case of hydrogen chloride (Exp. 56).

Water at 0° C. dissolves 1,300 times its volume of the gas, and at 15° C. 727 volumes. The aqueous solution is lighter than water, and in its most concentrated form has the specific gravity 0·884; it contains 36 per cent. by weight of the gas. The gas may be entirely expelled by boiling the solution. Two hydrates of ammonia have been obtained.

Ammonium hydroxide, $NH_3.H_2O$ or $(NH_4)OH$ melting at — 79° C.

And ammonium oxide, $2NH_3.H_2O$ or $(NH_4)_2O$ melting at 79° C.

Ammonia neither burns readily in air nor supports combustion, but a mixture of warm ammonia and oxygen burns with a greenish-yellow flame—

$$4\,NH_3 + 3\,O_2 = 2\,N_2 + 6\,H_2O.$$

If, however, red-hot platinum gauze is used as a catalyst the ammonia is converted to nitric oxide—

$$4\,NH_3 + 5\,O_2 = 4\,NO + 6\,H_2O.$$

In this way nitric acid can be obtained from ammonia, a method which was used extensively by Germany in the war.

Exp. 68. Gently warm a strong solution of ammonia in a wide-mouthed eight-ounce flask, and bubble oxygen gas through the solution at the same time. A mixture of ammonia and oxygen will pass out at the open mouth of the flask, and will burn when a light is applied to it.

Metallic oxides which are reduced in hydrogen also undergo reduction when heated in ammonia gas; the hydrogen of the ammonia combines with the oxygen of the oxide to form water, and nitrogen is set free.

245. Ammonium Salts.—Ammonia in presence of water is a strong alkali, and combines directly with acids to form ammonium salts; this can be well shown with hydrochloric acid gas.

Exp. 69. Fill two similar jars by displacement with ammonia and hydrochloric acid gas respectively, and cover the mouth of each jar with a glass plate. Now bring them mouth to mouth and withdraw the glass plates. The gases as they come into contact will combine, forming ammonium chloride, a fine white powder which remains for some time diffused throughout the jars.

$$\underset{\text{2 vols.}}{NH_3} + \underset{\text{2 vols.}}{HCl} = NH_4Cl.$$

Ammonium sulphate, $(NH_4)_2SO_4$, ammonium nitrate, NH_4NO_3, and other salts may be obtained by neutralising a solution of ammonia with the respective acids, and then evaporating to dryness on a water-bath.

The ammonium salts all contain the group of atoms NH_4, which in them plays the same part as an atom of a monovalent metal. NH_4 does not exist in the free state. Such a group of atoms, which enters into a series of compounds, is called a *compound radicle*. We have had an example of a compound radicle in the case of hydroxyl (OH). These two radicles combine together when ammonia gas dissolves in water, forming ammonium hydroxide, NH_4OH.

As the ammonium salts in solution strongly resemble the salts of potassium, they are more fully considered in *Inorganic Chemistry, Mainly Metals*, under the alkali metals. It will be well here, however, to summarise the effects of heat on ammonium salts, as in this respect they differ strikingly from the potassium salts which otherwise they so closely resemble.

When ammonium chloride is heated, it *apparently* sublimes unchanged, the vapour condensing again to ammonium chloride. It has been shown, however, that the vapour is

not that of ammonium chloride, but is a mixture of ammonia and hydrochloric acid,* which recombine on cooling—

$$NH_4Cl = NH_3 + HCl.$$

This dissociation is proved by measurement of the vapour density, and, more directly, by partially separating the two gases by diffusion.

The ammonium salts of less volatile acids, *e.g.* sulphuric and phosphoric acids, are also dissociated by heat, but in this case the volatile ammonia comes off alone, leaving the acid behind—

$$(NH_4)_2SO_4 = 2\,NH_3 + H_2SO_4.$$

The ammonium salts of the oxyacids of nitrogen are not dissociated but decomposed by heat, giving either nitrogen and water, or nitrous oxide and water—

$$NH_4NO_2 = N_2 + 2\,H_2O$$
$$NH_4NO_3 = N_2O + 2\,H_2O.$$

All ammonium compounds give off ammonia when heated with lime or caustic soda.

As already mentioned, ammonia combines directly with calcium chloride, the compound being represented by the formula $CaCl_2 \cdot 8\,NH_3$.

When ammonia is passed over heated sodium or potassium, hydrogen is liberated and sodamide or potassamide is formed—

$$2\,Na + 2\,NH_3 = 2\,NaNH_2 + H_2$$
$$2\,K + 2\,NH_3 = 2\,KNH_2 + H_2.$$

Excess of chlorine converts ammonia to *nitrogen trichloride*, NCl_3, an oily explosive liquid—

$$NH_3 + 3\,Cl_2 = NCl_3 + 3\,HCl.$$

If the ammonia is in excess the following reaction occurs (see page 245)—

$$8\,NH_3 + 3\,Cl_2 = N_2 + 6\,NH_4Cl.$$

Iodine or iodine-monochloride reacts with ammonia to give nitrogen iodide, a black compound which is highly explosive.

* If, however, the ammonium chloride is *absolutely dry*, it volatilises without dissociation.

246. Liquefaction of Ammonia by Pressure.—If ammonia gas is generated in quantity, and the receiver into which it passes is a closed vessel much smaller than the volume of the gas generated, it will be compressed and ultimately condensed by its own pressure to the liquid form. This is indeed the method of Faraday (see § 29), and a simple form of apparatus in which this principle is made use of is that of Carré Fig. 47). It consists essentially of a strong iron cylinder containing concentrated ammonia solution, as shown at A in the figure; this communicates with a receiver B, of relatively small volume, by means of the tube C. When A is surrounded by hot water, ammonia gas is given off freely and accumulates in the apparatus in such quantity that it condenses in the receiver B, which has been surrounded by cold water.

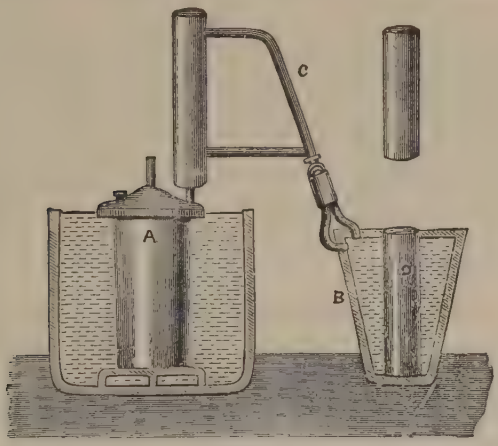


Fig. 47.

If we now reverse the arrangement and surround A with cold water, the liquid ammonia will boil very rapidly and pass back as gas into A, and this rapid transformation of liquid into gas will bring about a considerable depression of temperature in B. This vessel is provided with a space D, into which water may be introduced and frozen. By various applications

of this principle, liquid ammonia is used on a large scale for the preparation of ice, for refrigerating, and for obtaining low temperatures.

Ammonia is compressed in the pump A (Fig. 48), and is cooled in passing through the spiral C. In the chamber B cold water circulates and here the ammonia liquefies. The amount of liquid ammonia passing into the spiral F is regulated by the valve D. In coil F the liquid ammonia is under reduced pressure and therefore rapidly evaporates, taking heat from the bath E in doing so. The gas passes by means of H to the pump again. E contains calcium chloride solution which does not freeze. GG are vessels containing water which is frozen. Stirrers (not shown) are used to equalise the temperature throughout the bath E.

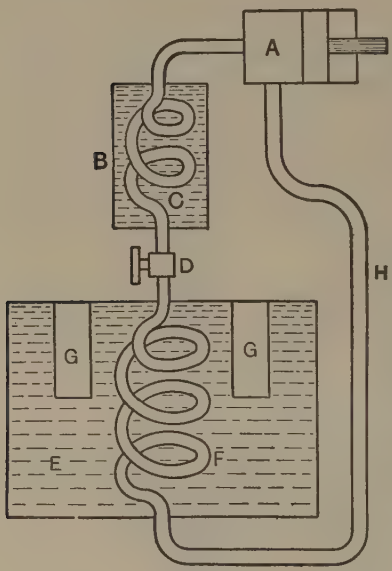


Fig. 48.

247. Composition of Ammonia. — The composition of ammonia may be determined by passing the gas through a red-hot tube containing copper oxide. The hydrogen is transformed into water, which may be collected and weighed in the manner already described (§ 111), and the volume of nitrogen which passes forward may also be ascertained—

$$3\,CuO + 2\,NH_3 = 3\,Cu + 3\,H_2O + N_2.$$

The *volume* of hydrogen may be readily calculated from the weight of water obtained.

A second method depends on the fact that when electric sparks are passed through gaseous ammonia it is slowly decomposed into its constituents. Dry ammonia is passed into a eudiometer over mercury, and its volume accurately measured. The sparks are then passed until no further increase in volume occurs; the final volume will be found to be just *double* the original volume. If, now, excess of oxygen be passed into the eudiometer and the spark passed, the hydrogen will combine with it and form water, which condenses, leaving nitrogen and the *excess* of oxygen added, two-thirds the diminution being the volume of hydrogen. The volume of nitrogen is found by subtracting the volume of hydrogen calculated from this diminution, from the volume of nitrogen plus hydrogen obtained after the first sparking.

This method is not very accurate owing to the fact that some of the nitrogen combines with oxygen, forming oxides of nitrogen. By the electrolysis of ammonia it may however be shown that the volume of nitrogen it contains is one-third that of the hydrogen. The experiment is performed in the following manner:—A saturated solution of common salt is prepared, and to this is added about one-tenth of its volume of strong ammonia. The solution is now introduced into a voltameter similar to that shown in Fig. 36, but fitted with carbon electrodes and submitted to the action of the current from six Bunsen cells. Nitrogen collects in one tube and hydrogen in the other, and the volumes will be found to be in the proportion 1 : 3.

One of the most convenient methods of proving the volumetric composition of ammonia depends upon the fact that chlorine is capable of removing the hydrogen from it with liberation of free nitrogen, as we saw in § 245. A long glass tube closed at one end is divided into three equal parts by india-rubber bands. It is next filled with chlorine by displacement of air, using a long narrow delivery tube, or at the pneumatic trough by displacement of chlorine water, and when quite full the mouth is closed by a cork carrying a small dropping funnel; this is done *before* the tube is removed from the trough so as to prevent any chlorine escaping.

The tube is now placed in an upright position and about 10 cub. cm. of strong ammonia solution are introduced into the funnel. This solution is allowed to flow into the tube drop by drop : the first drop which enters reacts with the chlorine with formation of a yellowish-green flame, and as more ammonia enters dense clouds of ammonium chloride are produced. When all the ammonia has been run in, a little dilute hydrochloric acid is introduced through the funnel to combine with the excess of ammonia. The gas which now remains in the tube is nitrogen under reduced pressure.

In order to bring it to atmospheric pressure the funnel is filled with dilute hydrochloric acid (see Fig. 49). On now opening the tap hydrochloric acid is sucked into the tube until the pressure is the same as that of the atmosphere. It will then be found that the liquid reaches to the second india-rubber band, *i.e.* the nitrogen occupies one-third of the tube.

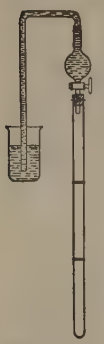


Fig. 49.

Now hydrogen and chlorine unite in equal volumes to form hydrochloric acid, so that the volume of hydrogen extracted from ammonia by the chlorine in the tube would just fill the tube. This hydrogen was originally in combination with the nitrogen left in the tube, so that the relative volumes of hydrogen and nitrogen in ammonia are in the ratio 1:3.

By combining with this result a knowledge of the density of ammonia we can completely prove its composition.

Since the volumes of nitrogen and hydrogen which combine to form ammonia are in the ratio 1 : 3, it follows by Avogadro's hypothesis that the number of molecules of nitrogen and hydrogen which combine are in the same ratio. But the molecules of these two elements each contain two atoms, and therefore—

$$\frac{\text{Number of atoms of nitrogen in ammonia}}{\text{Number of atoms of hydrogen in ammonia}} = \frac{1}{3}.$$

The formula of ammonia is, therefore, NH_3 or N_2H_6 or N_3H_9, etc.

Now the relative density of ammonia is 8·5 (H = 1), and consequently its molecular weight is $8{\cdot}5 \times 2 = 17$.

Let us take first the simplest formula, viz. NH_3. Since atomic weight of N = 14 and atomic weight of H = 1, the molecular weight of NH_3 is $14 + 1 \times 3 = 17$. This agrees with the number obtained from the density, so that NH_3 is the correct formula.

248. Detection and Estimation of Ammonia.—Ammonia may be recognised by its smell, action on litmus, and by giving dense white fumes of ammonium chloride when brought in contact with hydrochloric acid gas. With Nessler's solution ammonia gives a characteristic brownish coloration or precipitate, according to the amount of ammonia present; small quantities of ammonia can be estimated colorimetrically. Ammonia can be estimated by titration against an acid. The ammonia can be distilled into a known quantity of standard acid, and the excess of acid then estimated, or the substance can be heated with a known amount of standard alkali and the excess of alkali titrated.

249. Hydrazine, N_2H_4.—This substance is a colourless liquid boiling at 113·5° C. and melting at 1·4° C. It is prepared by the action of sodium hypochlorite upon a strong ammonia solution in the presence of glue—

$$NaOCl + 2\,NH_3 = NaCl + N_2H_4 + H_2O.$$

Hydrazine is readily soluble in water with evolution of heat; a compound hydrazine hydrate, $N_2H_4{\cdot}H_2O$, is first formed, and this then dissolves in the water. Hydrazine is a strongly basic substance, and forms salts with acids by direct addition, just as ammonia does, *e.g.* hydrazine sulphate, $N_2H_4 \cdot H_2SO_4$, hydrazine monohydrochloride, $N_2H_4 \cdot HCl$, and hydrazine dihydrochloride, $N_2H_4 \cdot 2\,HCl$. It is very poisonous and a very strong reducing agent, converting mercuric chloride into mercurous chloride and precipitating metallic silver from an ammoniacal solution of silver nitrate. The most important derivative is phenyl hydrazine, $C_6H_5.NH.NH_2$.

250. Hydrazoic Acid or Azoimide, HN_3, is a colourless liquid boiling at 37° C. Its sodium salt is formed by the action of nitrous oxide on sodamide, $NaNH_2$, the latter being prepared by the action of sodium on ammonia—

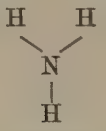
$$N_2O + 2\,NaNH_2 = NH_3 + NaN_3 + NaOH.$$

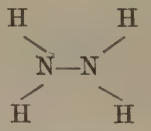
On distilling the sodium salt with sulphuric acid free hydrazoic acid is obtained—

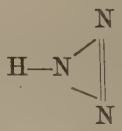
$$NaN_3 + H_2SO_4 = NaHSO_4 + HN_3.$$

Hydrazoic acid is readily soluble in water, producing a strongly acid solution in which many metals such as zinc, iron, copper, and aluminium readily dissolve with liberation of hydrogen and formation of the corresponding hydrazoates or azides of the metals. It is an unstable compound, exploding very easily when in the pure state; its salts are also explosive.

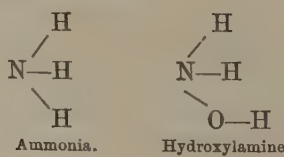
251. Constitution of the Hydrides of Nitrogen.—The constitutional formulae of the three hydrides of nitrogen are as follows, assuming hydrogen to be monovalent and nitrogen trivalent in each—


Ammonia.


Hydrazine.


Hydrazoic acid.

252. Hydroxylamine, NH_2OH.—This substance may be regarded as ammonia in which one hydrogen atom has been replaced by the hydroxyl group—


Ammonia. Hydroxylamine.

It is produced by the action of nascent hydrogen on nitric oxide or nitric acid—

$$NO + 3\,H \underset{\text{Nascent.}}{=} NH_2OH.$$

$$HNO_3 + 6\,H \underset{\text{Nascent.}}{=} NH_2OH + 2\,H_2O.$$

The reduction in the case of nitric acid may conveniently be brought about electrolytically as follows :—50 per cent. sulphuric acid is introduced into a cell divided into two compartments, one of which contains an amalgamated lead kathode. 50 per cent. nitric acid is gradually run into the kathodic compartment whilst a suitable current is passed through the cell. Nascent hydrogen is set free at the kathode and reduces the nitric acid to hydroxylamine, which combines with the excess of sulphuric acid to form the sulphate.

Anhydrous hydroxylamine may be prepared as follows :— Equivalent quantities of sodium methylate, CH_3ONa, and hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$, are dissolved in absolute methyl alcohol and the solutions mixed, when the following change takes place—

$$CH_3ONa + NH_2OH{\cdot}HCl = NH_2OH + CH_3OH + NaCl.$$

The sodium chloride being insoluble in alcohol is precipitated and may be removed by filtration. The filtrate is then fractionally distilled under diminished pressure; alcohol comes over first, then pure hydroxylamine.

Hydroxylamine is a white crystalline solid, melting at 33° C.; it is very deliquescent and dissolves readily in water, forming a strongly alkaline liquid. It is a mon-acid base, and like ammonia forms salts by direct combination with acids. Both hydroxylamine and its salts possess strong reducing properties; thus they precipitate gold and silver from solutions of these metals and convert cupric salts into cuprous oxide, ferric salts into ferrous salts, and sodium iodate into the iodide—

$$4\,CuSO_4 + 2\,NH_2OH + 8\,NaOH = 2\,Cu_2O + N_2O + 4\,Na_2SO_4 + 7\,H_2O.$$

In contact with such strong oxidising agents as potassium

permanganate and potassium dichromate, hydroxylamine undergoes decomposition with explosive violence, and it reacts violently with the halogens (chlorine causing it to inflame). Though as a rule acting as a reducing agent, hydroxylamine may under suitable conditions also act as an oxidising agent. For example, it oxidises warm zinc dust to zinc oxide, and in *alkaline* solution converts ferrous hydroxide into ferric hydroxide.

$$NH_2OH + 2\,Fe(OH)_2 + H_2O = 2\,Fe(OH)_3 + NH_3.$$

In both cases the hydroxylamine is reduced to ammonia.

QUESTIONS.—CHAPTER XVII.

1. Describe a method by which nitrogen may be obtained from air by removal of oxygen.

2. Give two methods for the preparation of nitrogen from ammonia or ammonium salts.

3. State the chief physical and chemical properties of nitrogen.

4. Describe an *accurate* method of determining the composition of the atmosphere by volume.

5. How may the composition of the air by weight be determined ?

6. A mixture of 25 c.cm. of air and 50 c.cm. of hydrogen is exploded in a eudiometer, and the volume of the residual gas is found to be 60·3 c.cm. ; find the percentage of oxygen in the air.

7. The percentage composition of air by weight being 76·058 nitrogen, 0·937 argon and 23·005 oxygen, find the composition by volume.

8. A litre of dry air is passed over heated copper and the increase in the weight of the copper found to be 0·297 grm. : find the percentage by weight of oxygen in the air. (1 litre of air weighs 1·293 grm.)

9. How would you show that air contains carbon dioxide, and what means would you adopt for ascertaining the amount of carbon dioxide present ?

10. How do the following impurities originate in air :—carbon dioxide, sodium chloride, ammonia, sulphurous acid ?

11. What agencies are at work which tend to remove such impurities as carbon dioxide and ammonia from the air ?

12. In what respect does a *mixture* of two gases, such as nitrogen and oxygen, differ in its behaviour from a *compound* of the two gases when shaken up in contact with water ?

13. What indications are usually shown that two gases which you have brought together have entered into combination ?

14. What reasons are there for supposing that the nitrogen and oxygen in air are mixed, not chemically combined ?

15. How is liquid air made and what are its properties ?

16. Write a short account of argon and the other inert elements present in the atmosphere.

17. What do you know of the history of ammonia ?

18. Give a general method by which ammonia may be obtained from nitrogenous animal or vegetable substances.

19. How would you prepare and collect dry ammonia ?

20. How is ammonia prepared industrially ?

21. How can it be shown that ammonia contains hydrogen ?

22. What experiments would you make to show that the composition of ammonia is rightly expressed by the formula NH_3 ?

23. Under what circumstances do nitrogen and hydrogen enter into combination, and under what circumstances is the compound so formed decomposed again without the intervention of chemical reagents ?

24. Write a short account of the compounds of nitrogen and hydrogen other than ammonia.

25. How is hydroxylamine prepared and what are its chief properties ?

CHAPTER XVIII.

COMPOUNDS OF NITROGEN AND OXYGEN.

In the following table is given the names of the oxides and oxyacids of nitrogen :—

Nitrous oxide,	N_2O.	Hyponitrous acid,	$H_2N_2O_2$.
Nitric oxide,	NO.		
Nitrogen trioxide, or nitrous anhydride,	N_2O_3.	Nitrous acid,	HNO_2.
Nitrogen peroxide,	N_2O_4.		
Nitrogen pentoxide, or nitric anhydride,	N_2O_5.	Nitric acid,	HNO_3.

253. Occurrence.—The higher oxides are formed in small quantity when the electric discharge takes place in a mixture of nitrogen and oxygen. These oxides, or nitrous and nitric acid formed from them, therefore occur in the atmosphere and in rain water ; waters contaminated by the drainage of surface soil, or by decaying nitrogenous organic matter, also contain similar products. In all such cases, owing to the difficulty of bringing about direct combination of nitrogen and oxygen, they are present in very minute quantities. Nitric acid or the nitrates being in most cases the source from which the oxides of nitrogen are derived, we shall treat these first.

Nitric Acid, HNO_3.

254. Preparation.—Nitric acid, being a volatile acid, is expelled from nitrates by the action of less volatile acids, such as concentrated sulphuric acid (or silica), and this reaction is made use of in its preparation, nitrate of potash or soda being usually employed.

Exp. 70. Introduce 20 grm. of potassium nitrate into a stoppered retort, and as much concentrated sulphuric acid as will just cover it. Apply a moderate heat, and presently the vapour of nitric acid will pass over and condense in the neck of the retort. The liquid may be collected in a small flask slipped over the mouth of the retort, and kept cool by means of a stream of cold water or a wet cloth. When about 10 c.cm. have been distilled over, or so soon as whitish fumes of sulphuric acid begin to appear, the experiment should be stopped—

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

255. Industrial Preparation.—Nitric acid is now manufactured on the large scale by three processes—

(1) From Chile saltpetre.

(2) From air by an electrical method.

(3) From ammonia by oxidation, using a catalyst.

(1) *From Chile Saltpetre.*—On the large scale, the native Chile saltpetre, $NaNO_3$, is employed, and the distillation is performed in large iron retorts, one of which is represented diagramatically in Fig. 50. The nitre and sulphuric acid are introduced through the opening A, and the cover D is then luted on. The nitric acid vapours escape through the pipe B, and are condensed either in a series of stoneware bottles, or by passing through a system of vertical earthenware pipes; in the latter case the liquid acid which collects at the bottom of the pipes is allowed to flow away into suitable receptacles.

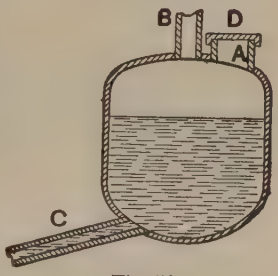


Fig. 50.

The change which takes place is represented by the equation—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

When the decomposition is completed the acid sodium sulphate, which is called *nitre-cake* is run off in the liquid state by the pipe C.

(2) *From the Atmosphere.*—The electrical process for the manufacture of nitric acid from the atmosphere is essentially

the production of oxides of nitrogen by the action of an electric discharge in air; these gases then dissolve in water to form nitric acid. This process was made commercially successful by two Scandinavian scientists, Birkeland and Eyde, in 1903.

$$N_2 + O_2 \rightleftharpoons 2\,NO - 43{,}200 \text{ calories.}$$

The reaction is reversible and endothermic, and thus a high temperature should favour the formation of nitric oxide. From the following table it will be seen that in order to secure a good yield, it is necessary to use a high temperature and then to "fix" the nitric oxide by rapidly cooling to 1,200°, below which temperature the decomposition of nitric oxide is a minimum.

Temperature.	Per cent. Volume of $N_2 + O_2$. $\rightleftharpoons$	Per cent. Volume of NO Formed.
1500° C.	99⅔	⅓
1922° C.	99	1
2307° C.	98	2
3000° C.	95·5	4·5

The practical details of the *Birkeland and Eyde Process* are as follows:—Air is passed through an electric arc which is spread into a large disc by means of a powerful electromagnet. An alternating current is used and the disc of arc from 6-8 ft. in diameter, is enclosed in a furnace lined with a refractory material (see Fig. 52). The electrodes EE (Fig. 51) consist of copper pipes which are cooled by a current of water.

The air is blown through AA and passes through holes in the fireclay lining, and is thus admitted to the disc-like arc (CC) laterally. The hot gases come out at D. The poles of the magnets are N and S, and BB are the windings.

In practice the product from the furnace consists of hot gases at a temperature of 1000° C., and contains 1·5 per cent.

of nitric oxide. These hot gases are cooled to 200° C. by passing through a series of steam boilers. During this cooling the nitric oxide combines with oxygen of the excess air which is present and forms nitrogen peroxide. The gas then passes into a series of absorption towers where it meets a stream of descending water or nitric acid of various strengths—

$$H_2O + 2\,NO_2 = HNO_2 + HNO_3.$$

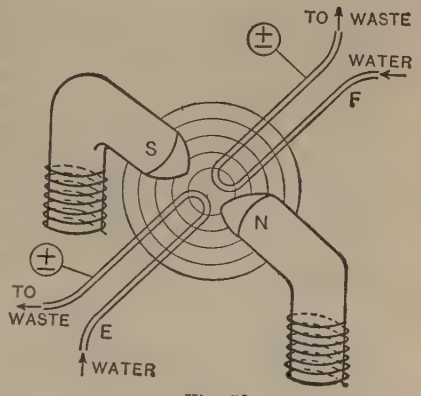


Fig. 51.

The acid obtained in the third tower is pumped to the top of the second tower, where it is allowed to circulate until it has reached a strength of 20 per cent. HNO_3. This acid is then sprayed from the top of the first tower, in which it circulates until a strength of 40-60 per cent. HNO_3 is obtained. Thus in the first tower the strongest acid is obtained, and it is free from nitrous acid which under these conditions is unstable and decomposes as follows:—

$$2\,HNO_2 = NO + NO_2 + H_2O.$$

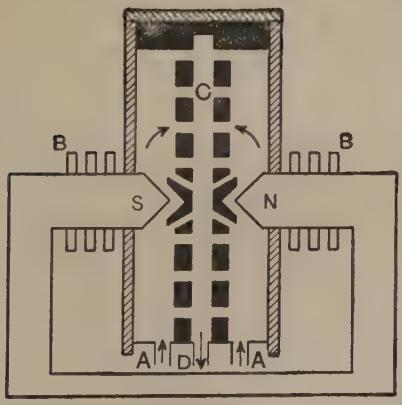


Fig. 52.

Most of the nitric oxide thus produced is oxidised to nitrogen peroxide by the oxygen present, so that ultimately practically all the

nitrogen peroxide originally produced is converted into nitric acid.

The fourth and fifth towers are sprayed with a solution of sodium carbonate, and the remaining oxides of nitrogen are absorbed to give a mixture of sodium nitrate and nitrite.

The Pauling Process is essentially the same as the Birkeland and Eyde Process described above.

(3) *From Ammonia.*—The cheap production of synthetic ammonia has enabled it to be used commercially for the manufacture of nitric acid.

The *Ostwald Process* depends on the oxidation of ammonia by air to nitric oxide by the use of red hot platinum gauze as a catalyst—

$$4\,NH_3 + 5\,O_2 = 4\,NO + 6\,H_2O.$$

The nitric oxide can then be absorbed as described under (2). Briefly the details of the working are as follows :—The ammonia and air are carefully purified and passed in certain proportions over a catalyst (platinum, etc.) at a temperature of 500° C. As the reaction is exothermic, heat is evolved during the reaction, and after a time the process proceeds automatically.

256. Purification of the Commercial Acid (obtained from (1)).—The chief impurities present in the commercial nitric acid obtained from (1) consist of chlorine and iodic acid (derived from the sodium chloride and sodium iodate in the saltpetre), sodium sulphate, sulphuric acid, and iron, carried over mechanically, and nitrogen peroxide (which is the principal cause of its red or yellow colour). The impure acid is fractionally distilled in glass retorts; chlorine and nitrogen peroxide come over in the first fraction, and when a small sample of the distillate collected separately fails to give the tests for chlorine, the receiver is changed and the greater part of the acid distilled off. The sulphuric acid, sodium sulphate, iron, and iodic acid remain behind in the retort. The purified acid still contains water and a little nitrogen peroxide. It is distilled with an equal volume of strong sulphuric acid, when anhydrous nitric

acid passes over at first into the receiver. To remove the nitrogen peroxide still present, a current of carbon dioxide is passed through the warm acid till it is colourless.

257. Fuming Nitric Acid.—This contains nitrogen peroxide in solution, and has a brownish colour. It is prepared industrially by the addition of starch to the nitrate in the retort, and by distilling strong nitric acid with strong sulphuric acid. It is a more powerful oxidising agent than the ordinary acid.

258. Properties of the Acid.—The pure acid is a colourless, fuming liquid, of specific gravity 1·53, boiling at 86° C. with partial decomposition into nitrogen peroxide, oxygen, and water. It is highly corrosive, and by contact instantly stains the skin yellow, more prolonged exposure giving rise to serious wounds. Dry straw and woody fibre are charred or even set fire to by contact with it. It mixes with water in all proportions, and if the dilute solution be concentrated in air at atmospheric pressure it becomes stronger until 68 per cent. of acid is present; it then distils unchanged at 121° C. under normal pressure, and has a density of 1·414. Similarly, on distilling an acid stronger than this, it gradually becomes weaker till it contains 68 per cent. of HNO_3, when it passes over unchanged. If the pressure is not normal the composition and boiling-point of the acid which distils unchanged have different values, as in the case of the halogen acids.

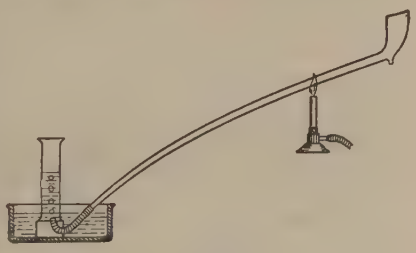


Fig. 53.

As already stated, pure nitric acid decomposes to some extent at its boiling-point; at higher temperatures this decomposition takes place very readily, as may be illustrated by the following experiment :—

Exp. 71. Support a clay pipe in the position shown in Fig. 53 by means of a retort-stand and clamp (not shown). Heat the tube strongly at a spot about 9 in. from the bowl by means of a Bunsen burner, and then pour about 5 c.cm. of strong nitric acid into the bowl. On reaching the heated part, decomposition takes place, and the weight of acid above pushes the gaseous products out through the stem of the pipe. The oxygen may be collected over water; the nitrogen peroxide being soluble goes into solution.

The equation representing the decomposition of nitric acid on heating is—

$$4\,HNO_3 = 2\,H_2O + 4\,NO_2 + O_2.$$

On account of the large percentage of oxygen which nitric acid contains (76 per cent.), and of the ease with which it parts with some of this oxygen, we should expect it to possess strong oxidising properties, and such is the case. Thus it readily transforms C, S, P, and I into CO_2, H_2SO_4, H_3PO_4, and HIO_3 respectively, whilst turpentine when mixed with it inflames. Nitric acid liberates sulphur from sulphuretted hydrogen and iodine from potassium iodide—

$$3\,H_2S + 2\,HNO_3 = 3\,S + 2\,NO + 4\,H_2O$$

$$6\,KI + 8\,HNO_3 = 3\,I_2 + 6\,KNO_3 + 4\,H_2O + 2\,NO.$$

Ferrous salts are oxidised to ferric salts.

259. Action on Metals.—Most metals dissolve readily in nitric acid with evolution of red fumes, the nitrate of the metal, or in some cases the oxide, being formed. It is only rarely that free hydrogen is one of the products of the reaction. We may suppose that the first action of nitric acid on a metal is to convert it into the nitrate with liberation of *nascent* hydrogen, but the latter is immediately oxidised to water by a further quantity of nitric acid. Thus, taking the case of copper, which reduces dilute nitric acid chiefly to nitric oxide, the two stages may be thus represented—

$$(1)\quad Cu + 2\,HNO_3 = Cu(NO_3)_2 + \underset{\text{Nascent.}}{2\,H}.$$

$$(2)\quad \underset{\text{Nascent.}}{3\,H} + HNO_3 = 2\,H_2O + NO.$$

On combining the two equations we get for the whole reaction—

$$3\,Cu + 8\,HNO_3 = 3\,Cu\,(NO_3)_2 + 2\,NO + 4\,H_2O.$$

The reaction may, however, be explained in another way, namely, by supposing that nitric acid first converts the metal into an oxide, itself undergoing reduction, and then the oxide reacts with a further quantity of nitric acid, producing a nitrate of the metal and water—

(1) $3\,Cu + 2\,HNO_3 = 3\,CuO + H_2O + 2\,NO.$

(2) $CuO + 2\,HNO_3 = Cu(NO_3)_2 + H_2O.$

It is beyond the scope of this book to discuss the relative merits of these two explanations.

The products of the reduction of nitric acid by metals may consist of any of the following substances : nitrogen peroxide, nitrous acid, nitric oxide, nitrous oxide, nitrogen, hydroxylamine and ammonia.

The exact course of the reaction depends upon the following factors :—

(1) The nature of the metal.

(2) The strength of the acid.

(3) The temperature.

(4) The concentration of the products in solution.

Thus we have seen that with moderately dilute acid copper forms chiefly nitric oxide ; with strong nitric acid, however, the main product is nitrogen peroxide—

$$Cu + 4\,HNO_3 = Cu(NO_3)_2 + 2\,H_2O + 2\,NO_2.$$

Similar equations may be written for silver, mercury, and lead.

Again, zinc with dilute nitric acid yields chiefly nitrous oxide, but with a somewhat stronger acid a large proportion of ammonia results—

(1) $4\,Zn + 10\,HNO_3 = 4\,Zn(NO_3)_2 + 5\,H_2O + N_2O.$

(2) $4\,Zn + 9\,HNO_3 = 4\,Zn(NO_3)_2 + 3\,H_2O + NH_3.$

The ammonia produced combines with the excess of nitric acid to produce ammonium nitrate—

$$NH_3 + HNO_3 = NH_4NO_3$$

so that equation (2) is more correctly expressed—

$$4\,Zn + 10\,HNO_3 = 4\,Zn(NO_3)_2 + 3\,H_2O + NH_4NO_3.$$

The relative amount of reduction which nitric acid has undergone when the products nitrogen peroxide, nitrous acid, etc., are formed, can be well illustrated in the following manner, regarding nascent hydrogen as the reducing agent :—

$$2\,HNO_3 + 2\,H = 2\,H_2O + 2\,NO_2.$$
$$2\,HNO_3 + 4\,H = 2\,H_2O + 2\,HNO_2.$$
$$2\,HNO_3 + 6\,H = 4\,H_2O + 2\,NO.$$
$$2\,HNO_3 + 8\,H = 5\,H_2O + N_2O.$$
$$2\,NHO_3 + 10\,H = 6\,H_2O + N_2.$$
$$2\,HNO_3 + 16\,H = 6\,H_2O + 2\,NH_3.$$

It will be noticed that the number of atoms of hydrogen required to reduce two molecules of nitric acid successively increases from nitrogen peroxide to ammonia.

The metals which *do* liberate free hydrogen from nitric acid are *magnesium* and *manganese*, the main products with the dilute acid being in both cases ammonia and hydrogen. When a metal such as mercury is capable of forming two nitrates, the lower one is produced when the metal is in excess, the higher when the acid is in excess. Tin with quite dilute acid gives stannous nitrate, but with stronger acid it behaves in an unusual manner, being converted into stannic oxide, SnO_2—

$$Sn + 4\,HNO_3 = SnO_2 + 4\,NO_2 + 2\,H_2O.$$

Antimony is similarly oxidised to antimony pentoxide, Sb_2O_5. Cold dilute nitric acid is without action on aluminium.

260. The Passive State.—Pure concentrated nitric acid does not attack iron, nickel, or tin.

It has been suggested that the acid coats them with a film of a higher oxide of the metal, which prevents the further action of the acid, rendering the metals " passive " ; another suggestion states that the cause is an electrical one. The phenomenon is, however, not yet perfectly understood.

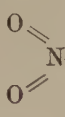
261. Aqua Regia.—The so-called " noble " metals, such as gold and platinum, are not acted upon by nitric acid of any strength, but readily dissolve in a mixture of hydrochloric

and nitric acids* which has for this reason been termed *aqua regia*.

The cause of the difference is that nitric acid liberates free chlorine, which, especially in the nascent state, readily attacks gold and platinum—

$$3\,HCl + HNO_3 = NOCl + Cl_2 + 2\,H_2O.$$

262. Constitution of Nitric Acid.—Nitric acid is represented by the constitutional formula—



263. The Nitrates.—These salts may be looked upon as nitric acid in which the hydrogen of the acid is replaced by a metal, thus—

HNO_3	KNO_3	$NaNO_3$	NH_4NO_3	$AgNO_3$.
$\left.\begin{matrix}HNO_3\\HNO_3\end{matrix}\right\}$	$Pb(NO_3)_2$	$Cu(NO_3)_2$	$Ca(NO_3)_2$	$Ba(NO_3)_2$.

They may be produced by the action of the acid on the metals or on their oxides, hydroxides, or carbonates.

Exp. 72. To a few cubic centimetres of *dilute* nitric acid contained in a porcelain basin add fragments of lead, and digest on a water-bath until the acid is saturated and no more of the metal will dissolve. Evaporate the clear solution till the salt crystallises when lead nitrate is obtained.

Exp. 73. Dilute 5 c.cm. of nitric acid with an equal bulk of water, and add a little litmus solution, which will become of a bright red colour. Now add ammonia solution little by little until the last drop turns the litmus blue, and concentrate the liquid to a point at which, when a drop of it is allowed to cool on the end of a glass rod, it crystallises. On standing, crystals of ammonium nitrate will be obtained.

All the nitrates are soluble in water: those of the alkali metals are the most stable, and those of the heavy metals

* *Aqua regia* is usually made by mixing nitric acid with four times its volume of hydrochloric acid.

the least stable. When strongly heated all undergo decomposition.

Nitrates of the heavy metals evolve oxides of nitrogen (generally NO_2) and oxygen, leaving an oxide of the metal—

$$2\,Pb(NO_3)_2 = 2\,PbO + 4\,NO_2 + O_2.$$

Nitrates of the alkali metals (K, Na) evolve oxygen, leaving a nitrite—

$$2\,KNO_3 = 2\,KNO_2 + O_2.$$

Ammonium nitrate decomposes in an exceptional way, forming nitrous oxide and water—

$$NH_4NO_3 = N_2O + 2\,H_2O.$$

Nitrates when heated naturally exert a powerful oxidising action on substances which may be mixed with them.

Exp. 74. Heat a few grammes of potassium nitrate in a test-tube until it fuses, and then drop into it one or two fragments of dry charcoal. The charcoal will ignite and burn with violence, being oxidised by the nitrate to CO_2.

Exp. 75. Repeat the experiment, introducing a few small shavings of lead; the lead will be oxidised at the expense of the nitrate and transformed into a yellowish powder, oxide of lead.

264. Tests for Nitrates.—(1) Nitrates when heated with sulphuric acid or silica give off nitric acid fumes, often accompanied by red fumes of nitrogen peroxide.

(2) Mix a solution of a nitrate with strong sulphuric acid, and add copper turnings; on warming red fumes will be given off.

(3) (A *sensitive* test). Mix a cold solution of a nitrate with a cold strong solution of ferrous sulphate, and pour gently down the side of the tube strong sulphuric acid: the latter sinks to the bottom, and a dark ring forms above it. The sulphuric acid liberates nitric acid from the nitrate, and the ferrous sulphate reduces the nitric acid to nitric oxide, which combines with more ferrous sulphate to form the dark-coloured solution.

(4) The addition of sulphuric acid with a *trace* of brucine to a solution of a nitrate gives a pink colouration. Under

similar conditions even a *trace* of nitric acid gives a blue colouration with diphenylamine.*

265. Estimation of Nitric Acid and Nitrates.—(1) Nitric acid can of course be estimated by titration with a standard solution of an alkali.

(2) Nitrates can be estimated by making use of the following reactions, and measuring the volume of nitric oxide evolved.

$$6\ Hg + 2\ HNO_3 + 3\ H_2SO_4 = 3\ Hg_2SO_4 + 2\ NO + 4\ H_2O$$

$$3\ FeCl_2 + HNO_3 + 3\ HCl = 3\ FeCl_3 + NO + 2\ H_2O.$$

(3) The nitrate can be reduced by the zinc-copper couple to ammonia which is then estimated.

266. Uses of Nitric Acid.—Nitric acid is largely used in the manufacture of a number of important substances such as sulphuric acid, nitroglycerine, guncotton, colours, and nitrates. Among the last may be mentioned silver nitrate, which is used in photography, strontium and barium nitrates, which are used in pyrotechny, and lead nitrate which is employed in calico-printing. Nitric acid is also used in Grove's and in Bunsen's electric batteries.

Nitrous Acid, HNO_2.

267. Preparation and Properties.—This acid is only known in dilute aqueous solution. It may be prepared by dissolving nitrogen trioxide in ice-cold water—

$$N_2O_3 + H_2O = 2\ HNO_2.$$

The aqueous solution gradually decomposes at ordinary temperature, and more rapidly on warming, according to the equations—

$$3\ HNO_2 = HNO_3 + 2\ NO + H_2O.$$

$$2\ HNO_2 \rightleftharpoons NO + NO_2 + H_2O.$$

It is a very weak acid and is displaced from its salts even by acetic acid.

* Diphenylamine is $(C_6H_5)_2NH$.

Nitrous acid is capable of acting both as a reducing agent and as an oxidising agent; as the former towards substances which readily give up oxygen, and as the latter towards those which readily take up oxygen. Thus it is rapidly converted into nitric acid by potassium permanganate, the latter being reduced and decolorised. In the presence of dilute sulphuric acid the reaction which takes place may be represented thus—

$$5\,HNO_2 + 2\,KMnO_4 + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 5\,HNO_3 + 3\,H_2O.$$

On the other hand, nitrous acid oxidises sulphur dioxide to sulphuric acid—

$$SO_2 + 2\,HNO_2 = H_2SO_4 + 2\,NO$$

and liberaties free iodine from potassium iodide. We may suppose that free hydriodic acid is first formed by double decomposition, and that this is then oxidised by the excess of nitrous acid—

$$KI + HNO_2 = KNO_2 + HI$$

$$2\,HI + 2\,HNO_2 = 2\,H_2O + 2\,NO + I_2.$$

268. Constitution of Nitrous Acid.—Nitrous acid is represented by the constitutional formulae—

or $O = N-O-H$.

269. Nitrites.—The nitrites of the alkali metals may be formed—

(1) By heating the corresponding nitrates, *e.g.*—

$$2\,NaNO_3 = 2\,NaNO_2 + O_2.$$

If the nitrate is heated with certain metals, such as lead, the decomposition is brought about more readily, the metal taking up the oxygen—

$$\underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\text{Lead.}}{Pb} = \underset{\text{Sodium nitrite.}}{NaNO_2} + \underset{\text{Lead oxide.}}{PbO}.$$

(2) By the action of nitrogen peroxide on the caustic alkalies. In this case nitrates are formed simultaneously—

$$2\,NO_2 + 2\,KOH = \underset{\text{Potassium nitrate.}}{KNO_3} + \underset{\text{Potassium nitrite.}}{KNO_2} + H_2O.$$

All nitrites are soluble in water, but silver nitrite, $AgNO_2$, is only sparingly soluble, and is formed as a white precipitate when a strong solution of silver nitrate is mixed with a strong solution of sodium nitrite.

270. Tests for Nitrites.—The usual methods for the detection of nitrites are as follows :—

(1) The evolution of red fumes (nitrogen peroxide) when the salt is warmed with sulphuric acid.

(2) The formation of a dark brown solution when a solution of ferrous sulphate is added to a solution of a nitrite, to which *dilute* sulphuric acid has been added (in some cases the addition of acid is unnecessary).

(3) The liberation of iodine from potassium iodide on the addition of an acid, *e.g.* sulphuric acid, and the decolorisation of potassium permanganate solution in presence of acetic acid.

(4) Meta-phenylenediamine* in acid solution gives a brown colouration even with traces of nitrous acid.

271. Estimation of Nitrous Acid and Nitrites.—(1) Nitrites can be estimated by reduction to nitric oxide or ammonia as described under nitrates (see § 265).

(2) Test 3 above may be used in the absence of other oxidisable compounds.

272. Hyponitrous Acid, $H_2N_2O_2$.—This acid may be prepared in two ways—

(1) By the action of a solution of hydrochloric acid in ether (whereby water is excluded) on silver hyponitrite (obtained as below)—

$$\underset{\text{Silver hyponitrite.}}{Ag_2N_2O_2} + 2\,HCl = 2\,AgCl + \underset{\text{Hyponitrous acid.}}{H_2N_2O_2}.$$

* Metaphenylenediamine is $C_6H_4(NH_2)_2$.

(2) By the interaction of hydroxylamine and nitrous acid—

$$\underset{\text{Hydroxylamine.}}{NH_2OH} + \underset{\text{Nitrous acid.}}{HNO_2} = \underset{\text{Hyponitrous acid.}}{H_2N_2O_2} + H_2O.$$

Pure hyponitrous acid is a white, crystalline, explosive substance. It is readily soluble in water, the solution slowly decomposing into nitrous oxide and water—

$$H_2N_2O_2 = H_2O + N_2O.$$

Hyponitrous acid is readily oxidised to nitric acid. It is a weaker acid than even HNO_2.

The acid has been proved to have the formula $H_2N_2O_2$, and not HNO, by determining its molecular weight by the lowering of freezing-point method (see *Inorganic Chemistry, Mainly Metals*).

273. Constitution of Hyponitrous Acid.—Hyponitrous acid is represented by the constitutional formula—

$$HO - N = N - OH.$$

274. Hyponitrites.—Hyponitrous acid is a dibasic acid, and forms both normal and acid salts, *e.g.* acid potassium hyponitrite, KHN_2O_2, and normal potassium hyponitrite, $K_2N_2O_2$.

The hyponitrites may be prepared by the careful reduction of nitrates or nitrites, a weak reducing agent such as sodium amalgam and water being used. Thus in the case of sodium nitrite we have—

$$2\,NaNO_2 + \underset{\text{Nascent.}}{4\,H} = Na_2N_2O_2 + 2\,H_2O.$$

The nascent hydrogen is formed by the action of water on the sodium in the amalgam. The equation representing the complete reaction is—

$$4\,NaNO_2 + 4\,NaHg_2 + 2\,H_2O = Na_2N_2O_2 + 2\,NaOH + 8\,Hg.$$

After reduction acetic acid is added to neutralise the solution and a solution of silver nitrate is added; silver hyponitrite is obtained as a yellow precipitate.

$$Na_2N_2O_2 + 2\,AgNO_3 = Ag_2N_2O_2 + 2\,NaNO_3.$$

Nitrogen Pentoxide, N_2O_5.

275. Nitrogen Pentoxide.—This is a white crystalline solid obtained by the action of a powerful dehydrating agent, such as phosphorus pentoxide, on nitric acid. Nitric acid of density 1·5 is introduced into a retort and well cooled by means of a freezing mixture. A quantity of phosphorus pentoxide equivalent to the acid used is gradually added, and on now gently warming the mixture nitrogen pentoxide distils over and collects in a cooled receiver as an orange-coloured liquid. Crystals of nitrogen pentoxide slowly separate and can be further purified by recrystallisation—

$$2\,HNO_3 + P_2O_5 = 2\,HPO_3 + N_2O_5.$$

A second method of preparation by which the substance was first obtained by Deville in 1849, is to pass dry chlorine over dry silver nitrate—

$$4\,AgNO_3 + 2\,Cl_2 = 2\,N_2O_5 + 4\,AgCl + O_2.$$

Nitrogen pentoxide enters into combination with water with great energy, reproducing nitric acid; it is therefore the anhydride of this acid. It is an unstable body, melting at 30° C. to form a yellow liquid with slight decomposition. If heated to its boiling point, 50° C., it decomposes. Nitrogen pentoxide is a strong oxidising agent.

Nitrogen Tetroxide or Peroxide, N_2O_4 or NO_2.

276. Preparation.—Nitrogen peroxide is formed on the direct combination of nitric oxide, NO, with oxygen—

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2.$$

The reaction is exothermic and reversible at temperatures above 500° C. and below 800° C.

It is usually prepared in the laboratory by heating lead nitrate—

$$2\,Pb(NO_3)_2 = 2\,PbO + 2\,N_2O_4 + O_2.$$

Exp. 76. Introduce 10 grm. of finely-powdered lead nitrate into a retort of "hard" glass (see Fig. 54) connected with a U-tube surrounded by a freezing mixture (pounded ice or snow and salt) and heat strongly. Red fumes are given off and condense in the U-tube to a colourless

liquid, N_2O_4. Remove the freezing mixture and note that as the temperature rises the liquid darkens in colour, and at ordinary temperatures is *orange yellow.*

Nitrogen peroxide is also formed to some extent when electric sparks are passed through a mixture of nitrogen and oxygen—

$$N_2 + 2\,O_2 = 2\,NO_2.$$

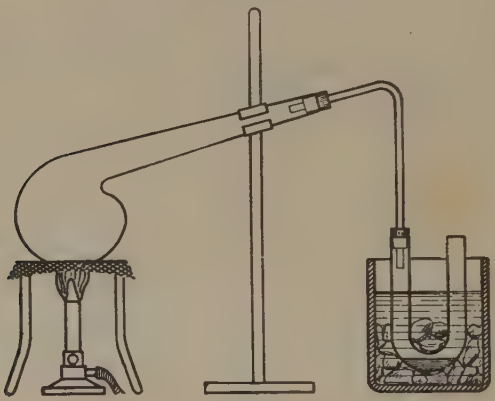


Fig. 54.

277. Properties.—The liquid obtained as in the experiment just described passes, on strongly cooling, into a colourless solid, melting at — 10° C. If, on the other hand, its temperature is further raised it continues to get darker, and at 22° C. boils, giving off a reddish-brown vapour; the vapour, in its turn, continues to darken with rise of temperature till it becomes almost black. This change in colour is accompanied by a corresponding change in composition. Thus at low temperatures (— 10° C.) nitrogen peroxide has the composition N_2O_4, and at 150° it has completely dissociated into NO_2 molecules, whilst at intermediate temperatures some of the molecules are N_2O_4, others are NO_2—

$$2\,NO_2 \underset{\text{Above } 150°.}{\overset{\text{Below } 150°.}{\rightleftharpoons}} N_2O_4$$

That this is the true explanation is proved by the changes in density which the gas undergoes with rise of temperature.

In the following table the values of the relative density (H = 1) are given for several different temperatures, and also the corresponding molecular weights:—

Temperature.	Relative Density.	Molecular Weight.
26·7°	38·3	76·6
60·2°	30·1	60·2
100·1°	24·3	48·6
135·0°	23·1	46·2
140·0°	23·0	46·0

Now the molecular weight of N_2O_4 is 92, and that of NO_2 is 46, from which it follows that at 140° C. the dissociation into NO_2 molecules is complete, but at 26·7° C. the greater part of the gas consists of N_2O_4 molecules. By means of the lowering of freezing-point method of determining molecular weights, it has further been shown that at low temperatures nitrogen peroxide is composed of N_2O_4 molecules.

Nitrogen peroxide is not a supporter of combustion in the ordinary sense, *i.e.* it extinguishes a lighted taper, but substances which burn in oxygen and give out sufficient heat to decompose the nitrogen peroxide will also burn in the latter. Thus brightly burning phosphorus continues to burn in the gas with a dazzling light. Nitrogen peroxide is an oxidising agent and converts moist sulphur dioxide into sulphuric acid—

$$SO_2 + H_2O + NO_2 = H_2SO_4 + NO,$$

and carbon monoxide into carbon dioxide even at ordinary temperatures. It also liberates iodine from solutions of potassium iodide. Nitrogen peroxide is decomposed by water, the exact course of the reaction depending on the conditions. With a small quantity of cold water, nitric and nitrous acids are produced, and in this way it acts as a mixed anhydride—

$$H_2O + 2\,NO_2 = \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Nitrous acid.}}{HNO_2},$$

but with hot water or with excess of water at ordinary temperature, the reaction proceeds thus—

$$H_2O + 3\,NO_2 = 2\,HNO_3 + NO.$$

This is what we might expect when we remember the ease with which nitrous acid decomposes into nitric acid and nitric oxide. During the solution of liquid nitrogen peroxide in water the liquid passes through a series of colour changes —blue, green, and orange. This is supposed to be due to the gradual solution of the nitrogen peroxide in the nitric acid formed. Of course, in the presence of sufficient water all the nitrogen peroxide is decomposed and the solution becomes colourless.

With the alkalies nitrogen peroxide forms a mixture of nitrate and nitrite—

$$2\,NaOH + N_2O_4 = NaNO_2 + NaNO_3 + H_2O.$$

The gas attacks many metals, such as mercury, copper, and iron. It is very poisonous.

Nitrogen Trioxide, N_2O_3.

278. Nitrogen Trioxide.—Nitrogen trioxide, N_2O_3, or nitrous anhydride, is obtained when nitric oxide is passed into liquid nitrogen peroxide, or when the two gases mix at temperatures below — 21° C.—

$$NO + NO_2 = N_2O_3.$$

A convenient laboratory method consists in heating nitric acid of specific gravity 1·25 with starch or arsenious oxide, and condensing the vapours formed in a vessel surrounded by a freezing mixture—

$$As_2O_3 + 2\,HNO_3 + 2\,H_2O = 2\,H_3AsO_4 + N_2O_3.$$

Prepared in this way it is a blue liquid which boils at —3° C. with partial decomposition. At temperatures above 0° C. it loses its blue colour and forms brown fumes of nitrogen peroxide. At — 21° the blue liquid is stable, and forms blue crystals at — 103° C. Baker, by taking special precautions to dry the liquid, was able to obtain a blue liquid which boiled at 43° C. without decomposition; the vapour density of the

gas formed showed that it contained the molecules N_4O_6 and N_2O_3.

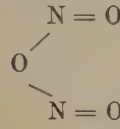
With ice-cold water nitrogen trioxide forms nitrous acid—

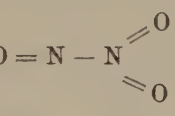
$$N_2O_3 + H_2O = 2\,HNO_2,$$

and with alkalies it forms a nitrite—

$$2\,NaOH + N_2O_3 = 2\,NaNO_2 + H_2O.$$

Nitrogen trioxide is thus nitrous anhydride. The constitution of the compound is not yet known with certainty; there is evidence for both the following suggestions :—





Nitric Oxide, NO.

279. Preparation.—Nitric oxide was first isolated by Priestley, in 1772, by the action of copper on nitric acid, and it is usually prepared in the laboratory by this method. The reaction, which we have already discussed under Nitric Acid, is—

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO.$$

Exp. 77. Introduce a few grammes of copper turnings into an 8-oz. flask provided with a thistle funnel and delivery tube, and add about 50 c.cm. of a mixture of equal parts of nitric acid and water. In a few moments gas begins to be evolved without the application of heat, and red fumes appear in the flask.

These red fumes are formed by the action of the nitric oxide on the oxygen contained in the flask; after a time the colour disappears as they are displaced, and the gas may then be collected over water at the pneumatic trough.

The gas so produced is not pure; it may contain other reduction products of nitric acid, such as nitrous oxide. The best method of preparing pure nitric oxide is to warm a mixture of ferrous sulphate and potassium nitrate with dilute sulphuric acid—

$$6\,FeSO_4 + 5\,H_2SO_4 + 2\,KNO_3 = 3\,Fe_2(SO_4)_3 + 2\,KHSO_4 + 4\,H_2O + 2\,NO.$$

Nitric oxide is prepared industrially on a large scale as explained in § 255.

280. Properties.—Nitric oxide is a colourless gas not very soluble in water, which dissolves about $\frac{1}{20}$th of its volume of the gas under ordinary conditions. Liquid nitric oxide boils at — 150° C. and freezes at — 167° C.

Nitric oxide by mere admixture with oxygen combines with it, as we have seen, giving rise to red fumes of nitrogen peroxide—

$$2\,NO + O_2 = 2\,NO_2.$$

Exp. 78. Expose a jar of the gas to air, and observe the red fumes.

Exp. 79. Pass oxygen little by little into a jar of the gas standing over water, allowing an interval to elapse between each addition. Red fumes will be formed, and these will dissolve in the water, which gradually rises in the jar. If the gas is pure and the oxygen be added in the proper proportion, the water will rise so as to completely fill the jar. A dilute solution of nitrous acid is thus formed, and may be shown to liberate iodine from potassium iodide, or to decolorise potassium permanganate.

Although nitric oxide is an endothermic compound it is the most stable of the oxides of nitrogen, and is only decomposed into its elements at about 1000° C. It does not support combustion except when sufficient heat is evolved to decompose it, the oxygen which is liberated being the actual supporter of the combustion. Thus a lighted taper, burning sulphur, and feebly burning phosphorus are extinguished by it, but fully ignited phosphorus continues to burn brightly.

Exp. 80. Try whether a lighted taper, burning sulphur and phosphorus when just lighted, will continue to burn in the gas; then try phosphorus which has become fully ignited.

Nitric oxide combines with chlorine in the presence of charcoal at 50° C. to form nitrosyl chloride, NOCl—

$$2\,NO + Cl_2 = 2\,NOCl,$$

a gas which is used extensively for bleaching.

Nitric oxide dissolves readily in a solution of ferrous sulphate, forming a brown compound, $FeSO_4 \cdot NO$. This is the compound forming the " brown ring " in the test for nitrates.

On gently warming, this compound dissociates into ferrous sulphate and nitric oxide which is evolved in a pure state.

281. Composition of Nitric Oxide.—When iron is heated in nitric oxide it combines with the oxygen and sets free the nitrogen. The gas first expands by the heat, and the iron then burns, forming triferric tetroxide, Fe_3O_4. On the completion of the reaction only nitrogen remains, and this gas will be found to occupy half the volume of the original gas. Hence one molecule of nitric oxide contains one atom of nitrogen, and its formula may be expressed N_1O_x. To determine the value of x we must ascertain the density of nitric oxide compared with hydrogen. It will be found to be 15, and since the hydrogen molecule, H_2, weighs 2, the molecule of nitric oxide must weigh $15 \times 2 = 30$, *i.e.* $N_1O_x = 30$. But $N_1 = 14$; therefore $O_x = 30 - 14 = 16$. Now the atomic weight of oxygen is 16, and therefore $x = 1$, *i.e.* the molecule of nitric oxide is represented by NO.

Nitrous Oxide, N_2O.

282. Preparation.—Nitrous oxide, N_2O, was first isolated by Priestley, in 1772, by the action of nitric oxide on moistened iron filings—

$$Fe + 2\,NO + H_2O = N_2O + Fe(OH)_2.$$

Later Berthellot, in 1785, obtained it by heating ammonium nitrate (below). Davy also investigated the gas and determined its composition.

Nitrous oxide is familiarly known as "laughing gas," because when breathed in small quantity it produces a feeling of exhilaration, a fact first discovered by Davy. Inhaled in larger quantities it is an anaesthetic, and renders the subject insensible to pain. It is for this reason employed in dentistry.

It has already been pointed out (§ 209) that when nitric acid (dilute) is acted upon by zinc, nitrous oxide is formed. It is more usual, however, to prepare it by heating ammonium nitrate, the decomposition being represented by the equation—

$$NH_4NO_3 = N_2O + 2\,H_2O.$$

The decomposition of ammonium nitrate is often attended with explosions, and a mixture of sodium or potassium nitrate and ammonia sulphate is more convenient.

Exp. 81. Introduce a mixture of 8 grm. of sodium nitrate and 17 grm. of ammonium sulphate into a 4-oz. flask and heat gently—just so as to bring about a steady and not too rapid evolution of the gas. Cold water dissolves about its own volume of the gas; it may, however, be collected over hot water.

283. Properties of Nitrous Oxide.—It is a colourless gas with an agreeable odour and taste. It condenses to a liquid which boils at $-90°$ C. and freezes at $-102°$ C. One hundred volumes of water dissolve 130 volumes of the gas at 0° C., 92 at 10° C., and 67 at 20° C.

It is easily decomposed by heat, and supports combustion almost as readily as oxygen.

Exp. 82. Plunge a glowing taper into a jar of nitrous oxide, and it will burst into flame just as it does in oxygen. Sulphur and phosphorus also burn in the gas with almost as much vigour as in oxygen, though if only feebly ignited they may be extinguished. To distinguish it from oxygen, pass nitric oxide into the gas; no red fumes will appear.

284. Composition of Nitrous Oxide.—The composition of the gas may be determined by the combustion of potassium or sodium in it and by an estimation of the density. The combustion experiment may be carried out in the same way as described for hydrogen bromide (§ 196).

It will be found that when the residual gas has cooled down to the ordinary temperature there is no change in volume, showing that nitrous oxide contains its own volume of nitrogen. The formula must therefore be N_2O_x. But the density is 22, corresponding to a molecular weight 44; therefore the weight of oxygen in a molecule of nitrous oxide is $44 - 2 \times 14 = 16$. It follows that $x = 1$, and the formula is N_2O.

The composition may also be determined by exploding with excess of hydrogen in a eudiometer, when the reaction is—

$$N_2O + H_2 = H_2O + N_2.$$

The residual gas consists of nitrogen and excess of hydrogen; the amount of the latter is estimated by exploding with excess

of oxygen when two-thirds of the diminution in volume represents the hydrogen present.

Compounds of Nitrogen with the Halogens.

285. Nitrogen Trichloride, NCl_3.—This is a very explosive yellow liquid produced by the action of chlorine on ammonium chloride solution—

$$3\,Cl_2 + \underset{\text{Ammonium chloride.}}{NH_4Cl} = 4\,HCl + \underset{\text{Nitrogen trichloride.}}{NCl_3}.$$

Nitrosyl chloride, NOCl. This is a yellow gas formed by the direct union of nitric oxide and chlorine (§ 280)—

$$2\,NO + Cl_2 = 2\,NOCl.$$

It is also produced, mixed with chlorine, when aqua regia is gently warmed. (See § 261 for the equation.) When cooled by a freezing mixture nitrosyl chloride readily condenses to a red liquid boiling at — 6° C., and solidifies to form blood-red crystals at — 65° C.

Nitrosyl chloride is decomposed by water with formation of nitrous and hydrochloric acids, and by caustic alkalies with formation of the corresponding salts of these acids—

$$NOCl + H_2O = HNO_2 + HCl.$$

$$NOCl + 2\,KOH = KNO_2 + KCl + H_2O.$$

With sulphuric acid it forms nitrosyl sulphuric acid and hydrochloric acid—

$$NOCl + H_2SO_4 = ON.O.SO_2.OH + HCl.$$

Nitrosyl bromide, NOBr, and *nitrosyl fluoride,* NOF, are also known and similar in properties to nitrosyl chloride.

Nitrogen iodide, $N_2H_3I_3$. When iodine acts on aqueous ammonia a brownish-black explosive powder is obtained having the composition represented by the formula $N_2H_3I_3$, and called *nitrogen iodide*—

$$5\,NH_3 + 3\,I_2 = N_2H_3I_3 + 3\,NH_4I.$$

The substance has been shown to have the constitutional formula $H_3N = NI_3$.

QUESTIONS.—CHAPTER XVIII.

1. How do you account for the occurrence of oxides of nitrogen, and the oxyacids or salts of these, in the air and in the soil ?

2. Discuss the industrial methods for the preparation of nitric acid.

3. Describe the manufacture of nitric acid from Chile nitre. What are the chief impurities in the commercial acid, and how are they removed ?

4. What is the effect of distilling (*a*) very dilute nitric acid, (*b*) pure nitric acid ?

5. Give striking experiments calculated to illustrate in regard to nitric acid, (*a*) its powerful oxidising action ; (*b*) its powerful solvent action.

6. What explanations have been given of the action of dilute nitric acid on copper ?

7. Compare the action of nitric acid of different strengths on the metals, zinc, copper, and tin. Give equations.

8. Explain what is meant by the *passive state*.

9. What is *aqua regia*, and on what does its special power as a solvent of metals depend ?

10. How would you obtain from nitric acid (*a*) hydrogen, (*b*) nitrogen (*c*) oxygen ?

11. How would you prepare the nitrates of lead and potassium, and obtain them in the form of crystals ?

12. Give an account of the action of heat on metallic nitrates.

13. Describe three tests which are characteristic of nitrates.

14. What are the chief uses of nitric acid ?

15. What is the action of heat on a solution of nitrous acid ?

16. Give examples (with equations) of (*a*) the oxidising action, (*b*) the reducing action of nitrous acid.

17. By what chemical reactions may nitrites be distinguished from nitrates ?

18. State what you know of hyponitrous acid and the hyponitrites.

19. How is nitric anhydride usually prepared, and what are its chief properties ?

20. How is the tetroxide of nitrogen obtained ? Discuss the action of heat on this substance.

21. Under what conditions does nitrogen peroxide become a supporter of combustion ?

22. What is the action of water on nitrogen peroxide ?

23. How is nitrogen trioxide prepared ? What are its properties ?

24. How may *pure* nitric oxide be obtained ? How would you demonstrate that its chemical formula is NO ?

25. What are the properties of nitric oxide, and how may it be distinguished from nitrous oxide ?

26. Give two methods for the preparation of nitrous oxide.

27. State the *physical* properties of nitrous oxide, and say how you would distinguish it from oxygen by chemical tests. In what respects does it resemble oxygen ?

CHAPTER XIX.

SULPHUR. HYDRIDES AND CHLORIDES OF SULPHUR.

Sulphur.

286. History.—The element sulphur has been known from time immemorial, as it exists free in volcanic districts. The word sulphur is derived from the Latin form of a Sanskrit word "Sulvari," which means "enemy of copper"; for the ancients said that sulphur "destroys" copper when the two are heated together. Sulphur was considered to be the "principle of fire." Geber, about 800, postulated that it was one of the two essential constituents of all metals, viz. sulphur and mercury; a theory that was later modified by Becher and Stahl in their "Phlogiston Theory." Lavoisier, in 1777, first recognised it as an element. The allotropic modifications of sulphur were first studied in detail by Mitscherlich, the discoverer of the important law of isomorphism.

287. Occurrence.—Sulphur is one of the comparatively few elements which occur in quantity in the uncombined condition. In Europe it is found in the neighbourhood of active or extinct volcanoes in Italy, Sicily, Iceland, etc., being usually associated with mineral matter. In Louisiana sulphur occurs in very large quantities a few hundred feet below the surface. In combination with hydrogen it is found as sulphuretted hydrogen in certain mineral springs, and with metals as mineral sulphides, such as iron pyrites, FeS_2; galena, PbS; zinc blende, ZnS; and cinnabar, HgS. Sulphates of calcium (gypsum) and barium (heavy spar) also occur in some localities in considerable quantity. We see then that sulphur, either free, or in combination is widely distributed.

288. Extraction.—Sulphur melts at 113° C., and in the molten condition can be run off from the earthy impurities and obtained in a state of moderate purity. The process is carried out as follows :—Impure native sulphur is stacked in a brick kiln on a sloping floor, vertical air spaces being left at intervals. The sulphur is lighted at the bottom; a small quantity burns and the heat produced melts out the rest. The melted sulphur runs down the sloping floor and collects in a trough placed to receive it.

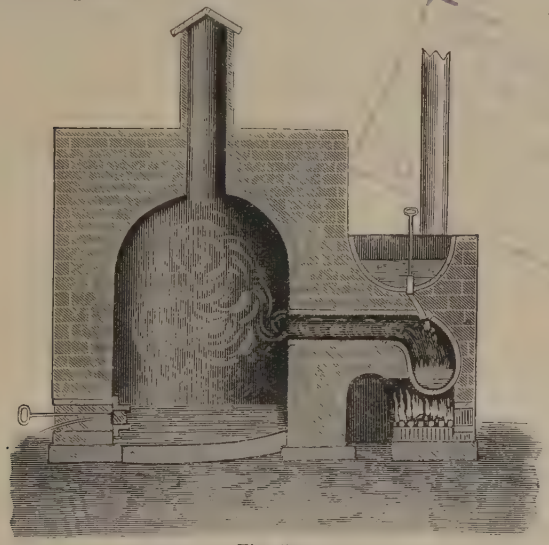


Fig. 55.

Sulphur boils at 444·6° C., giving off brownish-red vapours which readily condense again on cooling, and the further purification of the sulphur may be effected by distillation in an iron retort, the vapours being passed into a brick chamber where they condense (Fig. 55). At the outset when the chamber is cool the product obtained is a fine powder, called "flowers of sulphur," for just as water vapour at temperatures below zero (the melting-point of ice) condenses in the form of

snow, so in the case of sulphur there is formed by rapid cooling finely-divided sulphur.

When the temperature of the chamber rises above the melting-point of sulphur, about 113° C., the product of the condensation is *liquid* sulphur, and this is run off into moulds where it is cast into sticks known familiarly as " brimstone."

In the *Louisiana Process* the sulphur is obtained as follows:—A narrow boring is made to the sulphur deposit and superheated steam blown down. The sulphur is rendered molten and forced up another boring by means of compressed air. The molten sulphur is " laked," allowed to solidify, then broken up and sent into commerce. This product is much purer than the Silician sulphur, being about 99 per cent. pure.

289. Recovery of Sulphur: (1) *From Alkali-waste.* — " Alkali-waste," the residue from the soda-ash manufacture (see *Inorganic Chemistry, Non-Metals*), contains much calcium sulphide, and sulphur is recovered from it.

The waste is suspended in water and acted upon by carbon dioxide, when sulphuretted hydrogen is given off—

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S.$$

This gas is then burnt with just sufficient air to combine with the hydrogen and set the sulphur free—

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S.$$

This sulphur is generally used to form sulphur dioxide for the manufacture of sulphuric acid.

(2) *From Coal Gas.*—In the destructive distillation of coal sulphuretted hydrogen is evolved with the other gases. It is removed by passing the gases over wet ferric hydroxide—

$$Fe(OH)_3 + 3\,H_2S = Fe_2S_3 + 6\,H_2O.$$

The ferric sulphide thus produced is also used to make sulphur dioxide for the manufacture of sulphuric acid.

290. Properties of Sulphur.—Sulphur is a yellow solid, melting-point 113° C., boiling-point 444·6° C. Chemically it is a fairly active element, as will readily be seen in reading the ensuing pages.

291. Physical Changes of Sulphur under the Action of Heat.—The following experiment will show the physical changes which sulphur undergoes under the action of heat.

Exp. 83. Put about 10 grm. of sulphur in a wide test-tube, and heat it as evenly as possible in the flame of a Bunsen burner. At 113° C. it will be seen to melt, and at a slightly higher temperature it forms a limpid liquid of a pale yellow colour. As it gets hotter the liquid grows more viscid and darker in colour, till at 250° C. it becomes almost solid and nearly black. Above 250° C. it again becomes more mobile, and at 444·6° C. it boils and gives off a brownish-red vapour. Pour some of the sulphur at about 350° C. in a thin stream into a beaker of water, and note the production of plastic sulphur.

292. Allotropic Modifications of Sulphur.—Sulphur exists in several forms which show marked differences in their physical properties. These may be classified as follows :—

(1) *Crystalline Forms*—
Rhombic, Octahedral ; α sulphur ; or S_I.
Monoclinic, Prismatic ; β sulphur ; or S_{II}.
Monoclinic, Nacreous or S_{III}.
Monoclinic, Tabular or S_{IV}.

(2) *Amorphous Forms*—
Plastic Sulphur.
White amorphous ; or γ sulphur.
Yellow amorphous sulphur.

(3) *Colloidal Form*—
Colloidal ; or δ sulphur.

(4) *Fluid Forms*—
λ sulphur.
μ sulphur.
π sulphur.

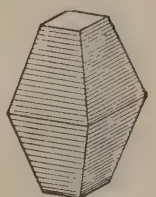


Fig. 56.

Rhombic Octahedral, α Sulphur or S_I.—Sulphur is found naturally in rhombic octahedra (see Fig. 56), and it is in this form that it separates out from solvents, such as carbon disulphide, on slow evaporation. The specific gravity of rhombic sulphur varies from 2·03 to 2·06.

Monoclinic, Prismatic, β Sulphur, or S_{II}.—Sulphur in this form is no longer rhombic, but monoclinic (Fig. 57) ; it is

also of lower specific gravity, 1·98, and melts at 119·25° C. instead of 113° C., and when left at the ordinary temperature for some time, breaks up and passes into the more stable rhombic form, as, indeed, all the modifications tend to do. It is soluble in carbon disulphide.

Exp. 84. Melt about 50 grm. of sulphur in a porcelain crucible, and allow it to cool until a crust forms at the surface; the crust is then pierced and the still liquid portion poured out. Beneath the crust and on the sides of the crucible will be found long prismatic needles of sulphur.

Monoclinic, Nacreous Sulphur, or S_{III}.—Nacreous sulphur is obtained in the form shown in Fig. 58 by suddenly cooling in a sealed tube, a supersaturated solution of sulphur in a solvent such as benzene, carbon disulphide, or alcohol; crystals resembling "mother of pearl" (French *nacré*, mother of pearl) separate out. It melts at 106·8° C.

Fig. 57.

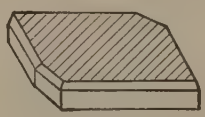


Fig. 58.

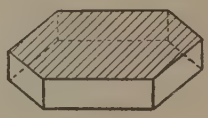


Fig. 59.

Tabular Sulphur or S_{IV}.—This is another form of monoclinic sulphur (see Fig. 59) and can be obtained by the same method as for the nacreous variety by keeping the temperature within the limits of 5° C., to 14° C.

It was stated above that prismatic sulphur slowly changes into rhombic sulphur. This change is a reversible reaction—

$$\text{Rhombic S} \overset{95\cdot6^\circ\text{ C.}}{\rightleftharpoons} \text{Monoclinic S},$$

$$\text{or} \quad S_I \rightleftharpoons S_{II},$$

and the two forms are in equilibrium at a temperature of 95·6° C. Above this temperature rhombic sulphur is unstable and slowly passes into the monoclinic variety; on the other hand, below this temperature monoclinic sulphur is unstable,

and slowly changes into the rhombic form. Thus 95·6° C is the "transition point" for α and β sulphur. Therefore by merely altering the temperature, one or other of the forms is produced, such substances being called *enantiotropic* (Greek, *enantios*, opposite, and *trepo*, I turn). Nacreous and tabular sulphur do not, however, exhibit this phenomenon, for they change into rhombic or prismatic sulphur according as the temperature is below or above 95·6°, and are said to be *monotropic* (Greek, *monos*, single, and *trepo*, I turn).

Plastic Sulphur.—As already stated, this form of sulphur is obtained by pouring sulphur at a temperature of 350° C. into cold water. Whilst in the crystalline form sulphur is brittle, in this condition, as the name implies, it can be moulded with the fingers, or drawn out into long flexible threads. Unlike the modifications previously described, it is insoluble in carbon disulphide : its specific gravity is 1·95. On standing, it slowly hardens and passes into the ordinary form of sulphur.

Plastic sulphur is an example of a *supercooled liquid*, that is a liquid which is very suddenly cooled to a temperature below its melting-point, so that it has no time to crystallise.

White Amorphous or γ Sulphur.—When hydrochloric acid is added to a solution of a polysulphide, *e.g.* calcium polysulphide or yellow ammonium sulphide, a white very finely-divided precipitate of amorphous sulphur is produced, called *milk of sulphur*. A part of this precipitate is insoluble in carbon disulphide and is called white amorphous, or γ sulphur. If sodium thiosulphate ($Na_2S_2O_3$) is used instead of a polysulphide, a similar white precipitate of sulphur is at first produced, but this gradually turns yellow, when it becomes soluble in carbon disulphide (being converted into the crystalline rhombic variety)—

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + S + SO_2 + H_2O.$$

Exp. 85. Make a moderately concentrated solution of sodium thiosulphate, or of an alkaline polysulphide (*e.g.* solution of yellow ammonium sulphide), and add a few drops of hydrochloric acid. The solution becomes turbid, and a white precipitate of "milk of sulphur" is produced.

Note that in the case of the thiosulphate the precipitate gradually turns yellow. Now add some carbon disulphide and shake up; the yellow crystalline precipitate dissolves, leaving a white precipitate of unchanged amorphous sulphur.

This variety of sulphur has a specific gravity 1·955.

Yellow Amorphous Sulphur. — "Flowers of sulphur" obtained as already described consists chiefly of small crystals of octahedral sulphur, but also contains a small percentage of an amorphous modification. The latter is insoluble in carbon disulphide, and can therefore be obtained by treating flowers of sulphur with this liquid, when the octahedral sulphur dissolves, and the amorphous portion remains behind as a light yellow powder of specific gravity 1·96. This form is also produced when disulphur dichloride (S_2Cl_2) is decomposed by water—

$$2\,S_2Cl_2 + 3\,H_2O = 4\,HCl + 3\,S + H_2O + SO_2.$$

Colloidal or δ Sulphur.—This is soluble in water and is obtained when solutions of sulphuretted hydrogen and sulphur dioxide are mixed—

$$SO_2 + 2\,H_2S = 2\,H_2O + 3\,S.$$

Liquid Sulphur.—When sulphur is heated to a temperature above its melting point, S_λ and S_μ are formed. Thus sulphur melts to a clear mobile liquid (mainly S_λ), but on further heating it becomes a dark viscous mass, S_μ. It has been found that by suddenly freezing these two liquids S_λ and S_μ, two solid modifications are produced, the former being soluble in carbon disulphide whilst the latter is insoluble. Another modification is formed when sulphur heated to 170° is suddenly chilled, and is called S_π.

The liquid forms S_λ and S_μ are related as follows :—

$$S_\lambda \overset{160°}{\rightleftharpoons} S_\mu.$$

It has been found that at each temperature $S\lambda$ and S_μ are in equilibrium, the quantities of each present in the equilibrium mixture depending on the temperature.

293. Proof that the Allotropic Modifications of Sulphur Consist of the Same Element.—On burning a known weight of any form of sulphur in oxygen and weighing the sulphur dioxide produced, it is found that in all cases the ratio of the weight of sulphur dioxide formed to that of sulphur burnt in 64 : 32, which agrees with the equation—

$$\underset{32}{S} + \underset{2 \times 16}{O_2} = \underset{32 + 2 \times 16 = 64}{SO_2}.$$

This proves that each of the different forms consists wholly of the same element. The experiment may be carried out as follows :—

A small fragment of sulphur (about 0·2 grm.) is weighed out accurately in a porcelain "boat" (A, Fig. 60). This is introduced into a piece of hard glass tubing in the position shown in the diagram. A series of bulbs, B, containing strong caustic potash solution, are weighed together with a small calcium chloride tube C, and then attached to the end of the tube remote from the porcelain boat. The other end of the tube is connected with a supply of dry oxygen. The boat is now gently heated by means of a Bunsen burner, and a slow current of oxygen is passed through the tube.

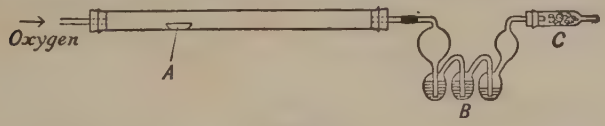


Fig. 60.

The sulphur burns, forming sulphur dioxide, which is absorbed in the potash bulbs. Any moisture driven out of the bulbs by the current of gas is absorbed by the calcium chloride in C, which, it will be remembered, was weighed along with the bulbs ; thus an error in the final weight of the bulbs due to loss of water vapour is avoided.

When all the sulphur has disappeared, and no more absorption is observed to be taking place in the bulbs, they are disconnected and re-weighed (with the calcium chloride tube), after cooling and passing dry air through them to displace oxygen. The increase in weight gives the weight of sulphur

dioxide. If any sulphur vaporises and condenses in the cooler part of the tube this must be gently heated by a Bunsen burner till it becomes oxidised.

294. Combination of Sulphur with other Elements.—Sulphur combines with many elements when heated with them. Thus it burns in oxygen at about 400° C., and it combines with carbon at a red heat, forming carbon disulphide, CS_2, while chlorine and hydrogen passed into boiling sulphur give disulphur dichloride, S_2Cl_2, and sulphuretted hydrogen respectively.

Many metals combine with sulphur when heated with it; for example, iron (see Exp. 5), silver, forming silver sulphide, Ag_2S, and copper, forming cuprous sulphide, Cu_2S.

Exp. 86. Heat sulphur to the boiling-point and until the upper part of the tube is filled with its vapour, and then plunge into it thin sheet copper, or Dutch metal; the metal glows, and enters into combination with the sulphur to form sulphide of copper.

295. Uses of Sulphur.—Sulphur is largely used in the arts for the production of matches, gunpowder, sulphuric acid, and as a source of sulphurous acid for bleaching wool, straw, and silk. It is used as a germicide, in medicine, and for vulcanising rubber.

296. Composition of the Sulphur Molecule.—At temperatures of 1000° C. and above, the density of sulphur vapour is 32 (H = 1), corresponding to a molecular weight of $2 \times 32 = 64$. Since the atomic weight of sulphur is 32, the molecule of sulphur at 1000° C. contains 2 atoms, *i.e.* it is represented by S_2. As the temperature falls, however, the density gradually increases till, at temperatures not far removed from the boiling-point of sulphur (*i.e.* at about 500° C.), its value is about three times as great as at 1000° C. This would correspond approximately to a molecule S_6; but there is no evidence to show that at any one temperature the molecules are all S_6; most probably molecules S_2, S_4, S_6, and S_8 are all present, the *mean* composition at one particular temperature corresponding to S_6. Below 500° C. the density goes on increasing still

further and becomes greater than 96 (= 3 × 32), showing that some of the molecules are more complex than S_6. At 2000° C. the vapour contains molecules corresponding to a monatomic molecule, S.

Hydrides of Sulphur.

297. The Three Combinations.—Hydrogen and sulphur combine to form three compounds two of which correspond to water and hydrogen peroxide, viz. hydrogen sulphide (H_2S) and hydrogen disulphide (H_2S_2). The third is hydrogen trisulphide (H_2S_3).

Hydrogen Sulphide or Sulphuretted Hydrogen, H_2S.

298. Occurrence.—Sulphuretted hydrogen occurs in solution in certain mineral waters (*e.g.* those at Harrogate), and is formed during the putrefaction of animal and vegetable matters which contain sulphur.

299. Preparation.—Hydrogen sulphide is formed when hydrogen is passed through boiling sulphur—

$$H_2 + S = H_2S,$$

and by mixing hydrogen and sulphur vapour at 500° C, the reaction being reversible and exothermic.

$$H_2 + S \rightleftharpoons H_2S.$$

The gas is most conveniently prepared in the laboratory by the action of dilute sulphuric acid, or dilute hydrochloric acid on ferrous sulphide—

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$
$$FeS + 2\,HCl = FeCl_2 + H_2S.$$

A convenient form of apparatus to use when a continuous supply of the gas is required is a Kipp's apparatus. Another arrangement suitable is shown in Fig. 61. The upper bottle contains the dilute acid, and the lower one the ferrous sulphide in lumps about the size of a walnut. The two bottles are connected by rubber tubing, on which is placed a clip, A.

The mouth of the lower bottle is fitted with a cork, through which passes a delivery tube provided with a stopcock, B, which is kept closed except when a supply of the gas is required. When this is the case the clip is loosened and a little acid allowed to run down on to the ferrous sulphide; the gas is led away by the delivery tube and passed through a wash-bottle containing a little water to remove impurities.

To stop the supply of gas, B is closed, and the ferrous sulphide bottle is raised so that the acid in it flows back into the acid bottle. H_2S cannot be collected over cold water as it is too soluble; and owing to its offensive nature, and to the fact that it is only slightly heavier than air, it should not be collected by displacement of air; also mercury is inadmissible because it attacks the gas. Since, however, the solubility in water rapidly decreases with rise in temperature, *hot* water may be used.

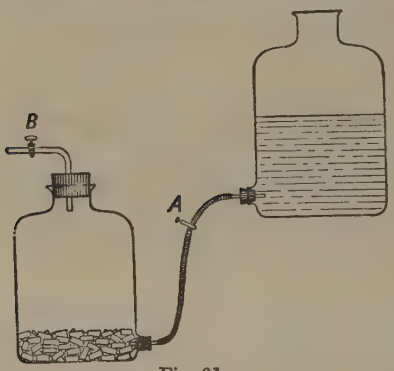


Fig. 61.

If only a small quantity of sulphuretted hydrogen is required, a Woulff's bottle provided with a thistle funnel and delivery tube may replace the apparatus above described.

The gas obtained in this way always contains free hydrogen on account of the iron present in the ferrous sulphide (which is prepared by heating iron and sulphur together). To obtain *pure* sulphuretted hydrogen, sulphide of antimony is heated in a flask with *concentrated* hydrochloric acid—

$$Sb_2S_3 + 6\,HCl = 2\,SbCl_3 + 3\,H_2S,$$

Antimony chloride.

or aluminium sulphide is acted upon by water—

$$Al_2S_3 + 6\,H_2O = 3\,H_2S + 2\,Al(OH)_3.$$

In the former case the gas is passed through a wash-bottle containing water to remove hydrochloric acid, and may then be collected as before. If *dry* sulphuretted hydrogen is required, the gas, after washing should be passed through a U-tube containing calcium chloride to absorb the water vapour (sulphuric acid cannot be used because it reacts with the gas).

300. Properties.—Sulphuretted hydrogen is a colourless gas with a disagreeable odour, and is poisonous if inhaled in quantity. It can be liquefied at a pressure of 17 atmospheres, or at a temperature of — 74° C., to give a product boiling at — 60° C., and which solidifies at — 83° C. Hydrogen sulphide is moderately soluble in water, which at 0° C. and 760 mm. pressure dissolves 4·7 times its volume of the gas, and at 20° C., 2·9 times its volume. The aqueous solution possesses the characteristic smell of the gas, and has a faintly acid reaction. Sulphuretted hydrogen burns with a blue flame, forming water vapour and sulphur dioxide in a free supply of oxygen or air, whilst in a limited supply of air free sulphur is formed—

$$2\,H_2S + 3\,O_2 = 2\,H_2O + 2\,SO_2$$
$$2\,H_2S + \quad O_2 = 2\,H_2O + 2\,S.$$

Exp. 87. Prepare a cylinder of sulphuretted hydrogen, apply a lighted taper to the mouth, and note that the gas burns with a pale blue flame, and that a gas (SO_2) is formed which has the suffocating odour of burning sulphur. There is usually a slight deposit of sulphur on the sides of the vessel due to the cooling of the gas, and to the difficulty of access of air in sufficient quantity to ensure complete combustion.

If the taper is passed within the cylinder in which the gas is burning, it will be extinguished, showing that sulphuretted hydrogen, like hydrogen, burns in air (or oxygen), but does not support the combustion of a taper.

Exp. 88. Fit the generating apparatus with a tube about 20 cm. long, drawn out to a fine jet. The gas may be lighted at the jet when all the air is expelled, and the presence of water in the products of combustion may be shown by holding a cool glass vessel over the flame. Also, by depressing the lid of a porcelain crucible into the flame, a deposit of sulphur may be obtained. Now heat the tube some distance away from the orifice with a Bunsen burner or spirit-lamp, and the gas will be decomposed by the heat, and a deposit of sulphur will form a little beyond the point where the heat is applied. Finally, extinguish

the flame, and allow the gas to impinge on a piece of filter-paper moistened with lead nitrate (or acetate); a dark stain will be produced owing to the formation of lead sulphide: by this test the presence of sulphuretted hydrogen may be detected even when present in very small quantities.

We have seen in the experiment just performed that sulphuretted hydrogen is easily decomposed by heat. It is also very readily broken up by the action of metals, many of which act upon it even at ordinary temperatures; the metal combines with the sulphur, and free hydrogen is liberated. The tarnishing of silver when exposed to the air of towns is an example of this; the air contains a small percentage of sulphuretted hydrogen produced during the combustion of coal, which usually contains a small quantity of iron pyrites (FeS_2); this H_2S in the air attacks the silver, producing a layer of silver sulphide, which is black.

On heating many metals in the gas the same change is brought about much more rapidly; tin and cadmium, for instance, very readily bring about the complete decomposition of a confined volume of the gas on the application of gentle heat—

$$Sn + H_2S = SnS + H_2.$$

As might be expected from the ease with which the gas is decomposed with liberation of hydrogen, sulphuretted hydrogen belongs to the class of reducing agents. For example, it reduces sulphuric acid to sulphur dioxide, ferric chloride to ferrous chloride, and nitric acid to nitrogen peroxide, according to the equations—

$$H_2S + H_2SO_4 = SO_2 + 2\,H_2O + S.$$

$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + 2\,HCl + S.$$

$$H_2S + 2\,HNO_3 = 2\,NO_2 + 2\,H_2O + S.$$

Again, potassium permanganate and potassium dichromate in the presence of dilute sulphuric acid are reduced to manganous sulphate and chromic sulphate respectively—

$$2\,KMnO_4 + 5\,H_2S + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,S.$$

$$K_2Cr_2O_7 + 3\,H_2S + 5\,H_2SO_4 = 2\,KHSO_4 + Cr_2(SO_4)_3 + 7\,H_2O + 3\,S.$$

In all these cases free sulphur is liberated. The action of the halogens on the gas has already been referred to in Chap. XIV.

301. Sulphides.—Sulphuretted hydrogen dissolves in water to give an acid solution. It behaves as a weak dibasic acid and gives with caustic potash, both potassium sulphide and potassium hydrogen sulphide—

$$2\,KOH + H_2S = K_2S + 2\,H_2O$$
$$KOH + H_2S = KSH + H_2O.$$

The sulphides are thus salts of hydrosulphuric acid, H.SH. The formation of the sulphides of the metals can conveniently be studied by experiment.

Exp. 89. Make a solution of sulphuretted hydrogen in water, and dip in it a blue litmus paper; it will be slightly reddened, showing that sulphuretted hydrogen is a weak acid.

Pour a few c.cm. of it into neutral solutions of copper sulphate, lead nitrate, nickel sulphate, zinc sulphate, calcium chloride, sodium chloride. The following results will be noticed :—

With copper sulphate, a black precipitate of cupric sulphide—

$$CuSO_4 + H_2S = \underset{\text{Cupric sulphide.}}{CuS} + H_2SO_4.$$

With lead nitrate, a black precipitate of lead sulphide—

$$Pb(NO_3)_2 + H_2S = \underset{\text{Lead sulphide.}}{PbS} + 2\,HNO_3.$$

With nickel sulphate, a black precipitate of nickel sulphide—

$$NiSO_4 + H_2S = \underset{\text{Nickel sulphide}}{NiS} + H_2SO_4.$$

With zinc sulphate, a white precipitate of zinc sulphide—

$$ZnSO_4 + H_2S = \underset{\text{Zinc sulphide.}}{ZnS} + H_2SO_4.$$

The same effects are produced by passing H_2S *gas* into solutions of the above salts.

In the case of calcium chloride and sodium chloride there will be no precipitate, owing to the fact that calcium sulphide, although only slightly soluble in water, would be soluble in the free acid formed, and sodium sulphide is readily soluble in water.

Now add some hydrochloric acid to the tubes containing the precipitates, and the sulphide of zinc will be found to dissolve, whilst those of copper, nickel, and lead will remain.

By such a method we may prepare many of the sulphides of the metals, and we can divide them into the following classes :—

(1) Sulphides insoluble in water and dilute mineral acids.

(2) Sulphides which are insoluble in water, but soluble in dilute mineral acids.

(3) Sulphides which are soluble even in water.

The precipitate may be separated by filtration from the solution which remains, and it is possible in this way to separate any member or members of one of these classes from those of another class.

Many of the sulphides may also be prepared by mixing the metal (preferably in a finely-divided condition or in filings) intimately with excess of powdered sulphur and heating in a porcelain crucible until the portion of sulphur over and above that which will enter into combination with the metal is volatilised. Access of air or of gases which may act upon the sulphide is to be avoided.

When strong aqueous ammonia is saturated with sulphuretted hydrogen the product consists of a solution of ammonium sulphide $(NH_4)_2S$, ammonium hydrogen sulphide, $NH_4 \cdot HS$, and ammonium hydroxide ; this solution is known as "ammonium sulphide." On allowing it to stand in contact with the air it undergoes partial oxidation with formation of free sulphur, which then combines with more ammonium sulphide to form polysulphides of the general formula $(NH_4)_2S_x$, where x may be as high as 9. These polysulphides are yellow, and so the solution of ammonium sulphide which is colourless at first gradually turns yellow and is then known as "yellow ammonium sulphide." Yellow ammonium sulphide is largely employed as a reagent in qualitative analysis.

Some sulphides dissolve in sodium sulphide or ammonium sulphide to form soluble thio-salts, *e.g.*—

$$As_2S_3 + 3\,(NH_4)_2S = 2\,(NH_4)_3AsS_3 \text{ ammonium thioarsenite}$$

$$SnS_2 + Na_2S = Na_2SnS_3 \text{ sodium thiostannate.}$$

302. Tests for Sulphides.—(1) Warm the substance with dilute sulphuric acid; *most* sulphides are decomposed with the evolution of sulphuretted hydrogen, *e.g.*—

$$\underset{\text{Ferrous sulphide.}}{FeS} + H_2SO_4 = \underset{\text{Ferrous sulphate.}}{FeSO_4} + H_2S.$$

The sulphuretted hydrogen may be detected by its odour or by its action on paper moistened with a solution of lead acetate, $Pb(C_2H_3O_2)_2$.

(2) Mix a little of a dry sulphide with sodium carbonate and heat strongly on charcoal with the blowpipe flame. Sodium sulphide is formed, and may be recognised by the fact that when a little of the product is placed on a silver coin and moistened, a brown stain is produced. All sulphides react in this way.

303. Composition of Sulphuretted Hydrogen.—When sulphuretted hydrogen is heated alone, or with metallic tin, it yields its own volume of hydrogen. The gas and tin are heated in a glass tube closed by a cork. When the tube has cooled the cork is removed under water. No gas escapes and water does not rise in the tube. By Avogadro's Law it follows that one molecule of sulphuretted hydrogen contains one molecule, *i.e.* two atoms, of hydrogen. Call the number of atoms of sulphur in the gas x; then the formula for sulphuretted hydrogen may be written H_2S_x. The simplest way to find x is to determine the molecular weight of sulphuretted hydrogen from its density. It is found that the relative density of the gas is 17 (H = 1); the molecular weight is, therefore, $2 \times 17 = 34$, and so

Molecular weight of sulphuretted hydrogen	=	34
Weight of hydrogen in a molecule of sulphuretted hydrogen	=	2
,, ,, sulphur ,, ,, ,,	=	32

But 32 is the atomic weight of sulphur; hence the molecule of sulphuretted hydrogen contains one atom of sulphur, *i.e.* $x = 1$, and the formula becomes H_2S.

304. Hydrogen Disulphide, H_2S_2. Hydrogen Trisulphide, H_2S_3.—These are oily liquids which separate out when a saturated solution of sulphide of calcium is gradually poured (stirring constantly) into a large excess of well cooled hydrochloric acid, diluted with twice its volume of water; sulphur is also liberated—

$$CaS_5 + 2\,HCl = CaCl_2 + 3\,S + H_2S_2.$$

By the fractional distillation of the oily liquid under reduced pressure two sulphides are obtained, *hydrogen disulphide*, H_2S_2, and *hydrogen trisulphide*, H_2S_3.

Hydrogen disulphide bears marked resemblance to hydrogen peroxide in its chemical properties. It forms persulphides corresponding in character to the peroxides, and acts as a bleaching agent. It boils at 74°C., is very unstable, and on gently heating readily breaks up into sulphuretted hydrogen and sulphur, just as hydrogen peroxide breaks up into water and oxygen.

The composition of hydrogen disulphide cannot be determined by estimating the amount of sulphur contained in it because it always contains excess of dissolved sulphur. Hydrogen disulphide, however, forms a compound with strychnine, the exact composition of which has been ascertained, and which on decomposition yields hydrogen disulphide. This compound consists of two molecules of strychnine combined with three molecules of H_2S_2. It is probable, therefore, that the formula H_2S_2, corresponding to H_2O_2, is correct.

Hydrogen trisulphide is similar in properties to the disulphide; it boils at 69° C. under a pressure of 2 mm.

Sulphur and the Halogens.

305. The Various Combinations.—Sulphur combines with the halogens to form the following compounds :—

SF_6	sulphur hexafluoride.
S_2Cl_2	,, monochloride.
SCl_2	,, dichloride.
SCl_4	,, tetrachloride.
S_2Br_2	,, monobromide.

Sulphur Hexafluoride, SF_6, is formed by the direct union of sulphur and fluorine. It is a colourless, odourless gas, inert and stable, and solidifies at — 55° C.

Sulphur Monochloride or *Disulphur Dichloride*, S_2Cl_2, is obtained when perfectly dry chlorine is brought into contact with sulphur vapour, by being passed over sulphur heated in a retort. The product is condensed in a receiver fitted to the mouth of the retort and kept cool by water (see Fig. 62).

Disulphur dichloride is a brownish-yellow liquid which boils at 138° C. and solidifies at — 76° C.; it fumes in moist air, and is decomposed by water; it readily dissolves sulphur, and the solution is then used in the vulcanisation of rubber. Disulphur dichloride was used extensively during the war for the preparation of "mustard gas."

Sulphur Dichloride, SCl_2, *and Sulphur Tetrachloride*, SCl_4.—When chlorine is passed into chloride of sulphur kept cool in ice, sulphur dichloride, SCl_2, is formed, and if the temperature is kept sufficiently low (— 22° C.) a further addition of chlorine takes place, and sulphur tetrachloride, SCl_4, is obtained. The dichloride and tetrachloride are both liquids which on heating readily give up chlorine, leaving behind S_2Cl_2.

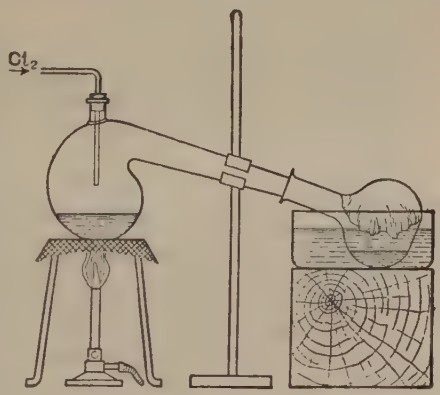


Fig. 62.

Sulphur Monobromide or *Disulphur Dibromide*, S_2Br_2, is formed as a red liquid by the direct combination of its elements.

QUESTIONS.—CHAPTER XIX.

1. How is sulphur obtained industrially ?

2. Under what conditions are "flowers" of sulphur and "milk" of sulphur formed ?

3. Describe the physical changes through which sulphur passes when it is heated in the absence of air.

4. Compare and contrast the allotropic modifications of sulphur.

5. Describe the preparation of (*a*) prismatic sulphur, (*b*) plastic sulphur, (*c*) rhombic sulphur.

6. What is the action of sulphur vapour on heated copper, iron, oxygen, hydrogen, and chlorine respectively ? Give equations representing the changes which occur.

7. How would you prove that octahedral and prismatic sulphur consist of the same element ?

8. Discuss the composition of the sulphur molecule at different temperatures.

9. In what proportions does hydrogen combine with sulphur ? Is there any analogy between the compounds so formed and those of hydrogen with oxygen ?

10. How would you prepare and collect a specimen of *pure dry* sulphuretted hydrogen ?

11. What products are obtained by burning sulphuretted hydrogen (*a*) in a limited supply of air, (*b*) in excess of air ?

12. Give examples with equations of the reducing action of sulphuretted hydrogen.

13. What is the action of sulphuretted hydrogen on acid solutions of (*a*) silver nitrate, (*b*) copper sulphate, (*c*) lead nitrate ? Give equations showing the changes which take place.

14. How would you show (*a*) that sulphuretted hydrogen contains hydrogen and sulphur, (*b*) that it contains these elements in the proportions represented by the formula H_2S ?

15. What is the composition of "yellow ammonium sulphide" ?

16. How is hydrogen disulphide prepared and what are its chief properties ?

17. What compounds does sulphur form with chlorine, how are they prepared, and what are their properties ?

CHAPTER XX.

OXIDES, OXYACIDS, AND OXYCHLORIDES OF SULPHUR.

306. The Various Compounds.—Sulphur forms four compounds with oxygen, namely, sulphur dioxide, SO_2, sulphur trioxide, SO_3, sulphur sesquioxide, S_2O_3, and sulphur heptoxide, S_2O_7. Two of these oxides, SO_2 and SO_3, combine with water to produce corresponding acids, sulphurous acid, H_2SO_3, and sulphuric acid, H_2SO_4, and they are therefore the anhydrides of these acids. The other two oxides do not produce the corresponding acids on treatment with water, though these acids can be obtained by other methods. A list of the oxyacids of sulphur is—

Sulphurous acid	H_2SO_3
Sulphuric acid	H_2SO_4
Pyrosulphuric acid	$H_2S_2O_7$
Thiosulphuric acid	$H_2S_2O_3$
Hydrosulphurous acid	$H_2S_2O_4$
Permonosulphuric acid	H_2SO_5
Perdisulphuric acid	$H_2S_2O_8$
The thionic acids	$H_2S_xO_6$

In the thionic acids $x = 2, 3, 4, 5$, or 6.

Sulphur Dioxide, SO_2.

307. History.—Sulphur dioxide, though its smell at least must have been long known, was not isolated until Priestley, about 1774, accidentally found that the gas is produced by the action of hot strong sulphuric acid upon mercury. Later, in 1777, Lavoisier showed that it is an oxide of sulphur.

308. Preparation.—When sulphur burns in air or oxygen, sulphur dioxide is formed, and for purposes in which admixture with nitrogen or the excess of oxygen is of no moment, the gas may be prepared by this method. On the manufacturing scale, indeed, sulphur dioxide is sometimes so obtained, though more usually a sulphide containing a large proportion of sulphur, such as iron pyrites, FeS_2, is employed (see § 317).

When the gas is required in a tolerably pure condition the following method is applicable :—

Exp. 90. About 20 grm. of metallic copper are placed in an 8-oz. flask provided with a thistle funnel and delivery tube, and 50 c.cm. of concentrated sulphuric acid are poured down the funnel. The flask is then heated on a sand-bath, moderating the heat so soon as the action commences. The reaction which takes place is a complex one, but consists essentially in the reduction of the sulphuric acid by copper. The latter is converted chiefly into $CuSO_4$ and Cu_2S—

$$Cu + 2\,H_2SO_4 = CuSO_4 + SO_2 + 2\,H_2O.$$

Mercury, charcoal, or sulphur may be substituted for copper, but in the case of charcoal the gas which passes off is mixed with carbon dioxide—

$$Hg + 2\,H_2SO_4 = SO_2 + 2\,H_2O + HgSO_4$$
$$C + 2\,H_2SO_4 = CO_2 + 2\,H_2O + 2\,SO_2.$$

With sulphur the reaction is—

$$S + 2\,H_2SO_4 = 2\,H_2O + 3\,SO_2,$$

sulphur dioxide being formed both from the sulphur itself and from the sulphuric acid used. Sulphites, bisulphites, or thiosulphates when treated with a mineral acid yield sulphur dioxide—

$$Na_2SO_3 + 2\,H_2SO_4 = 2\,NaHSO_4 + H_2O + SO_2$$
$$NaHSO_3 + HCl = NaCl + H_2O + SO_2$$
$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + H_2O + SO_2 + S.$$

Sulphur dioxide being very soluble in water cannot be collected over this liquid; mercury may, however, be used, but as the gas is more than twice as heavy as air it may be conveniently collected by displacement of air. Several jars may be filled with it, and its properties demonstrated by the experiments given below.

309. Properties.—Sulphur dioxide is a heavy, colourless gas having a suffocating odour. At 760 mm. pressure water at 0° C. dissolves 80 times its volume of the gas, and at 10° C. 56 times its volume, the solution having an acid reaction; on cooling the solution crystals of a hydrate, $SO_2 \cdot 7\ H_2O$, can be obtained. Sulphur dioxide condenses to a liquid under ordinary atmospheric pressure at — 8° C., and under 2 atmospheres pressure at 0° C. It can therefore be readily liquefied by passing the gas into a vessel surrounded by a freezing mixture of ice and salt. Liquid sulphur dioxide is usually contained in "siphons"; when the valve is loosened the gas is obtained.

Exp. 91. Put a lighted taper into a jar of the gas; it will be extinguished, nor will the gas itself burn. Metallic potassium when previously ignited will, however, burn at the expense of the oxygen in this gas.

Exp. 92. Show the great solubility of the gas by the method used in Exp. 56, or by passing the gas through 10 c.cm. of water until a saturated solution is obtained. Note the acid properties of the solution, and that it possesses the odour of the gas.

310. Reducing Action of Sulphur Dioxide.—Sulphur dioxide is a strong reducing agent; its powers as an antiseptic and as a medium for bleaching silk, straw, and wool are due to its affinity for oxygen. Chlorine bleaches in consequence of its bringing about the oxidation of the colouring matter; sulphur dioxide bleaches, on the contrary, in consequence of its reducing action. The one liberates *oxygen* from water—

$$Cl_2 + H_2O = 2\ HCl + O$$

the other liberates *hydrogen*—

$$H_2SO_3 + H_2O = H_2SO_4 + 2\ H.$$

The nascent hydrogen produced then combines with the colouring matter to produce a colourless compound. In many cases the colour is restored by exposure to air, when the oxygen of the air oxidises the colourless compound back to the original coloured substance. In some cases of bleaching by sulphur dioxide the coloured compound *combines directly with* SO_2; in such cases the colour may be restored by the addition of an acid which decomposes the colourless addition

product with evolution of sulphur dioxide. The SO_2 addition product may also be acted upon by the oxygen and moisture of the air, whereby the SO_2 is converted into sulphuric acid and the coloured compound again set free.

Exp. 93. Throw some green leaves into a solution of sulphur dioxide; they are bleached. Now add a few drops of strong sulphuric acid; the colour is restored. Bleach some more of the leaves in the same manner, remove them from the solution, and leave them exposed to the air for some time. The colour will gradually return.

It must be noted that an aqueous solution of sulphur dioxide does not undergo decomposition in the complete absence of air or other oxidising agent; water and sulphur dioxide do not react to give sulphuric acid and hydrogen unless there is some substance present to take up the hydrogen. In the presence of air the solution gradually absorbs oxygen, and the following change takes place—

$$2\,SO_2 + 2\,H_2O + \underset{\text{From the air.}}{O_2} = 2\,H_2SO_4.$$

Sulphur dioxide reduces iodic acid or iodates to iodine—

$$2\,HIO_3 + 5\,SO_2 + 4\,H_2O = I_2 + 5\,H_2SO_4.$$

Another good example of the reducing action of sulphur dioxide is its power of converting ferric salts into ferrous salts. Thus ferric sulphate is reduced to ferrous sulphate, and ferric chloride to ferrous chloride—

$$Fe_2(SO_4)_3 + SO_2 + 2\,H_2O = 2\,FeSO_4 + 2\,H_2SO_4$$
$$2\,FeCl_3 + SO_2 + 2\,H_2O = 2\,FeCl_2 + H_2SO_4 + 2\,HCl.$$

Potassium permanganate and potassium chromate are also readily reduced, the change being rendered conspicuous by the alterations in colour which result, the purple permanganate being decolorised, and the yellow chromate turned green.

Exp. 94. Add a solution of sulphur dioxide in water to solutions of potassium permanganate and potassium chromate respectively. Note the colour changes; they may be used as tests for sulphur dioxide, both in the gaseous state and in solution. Potassium chromate is more usually employed for this purpose than potassium permanganate.

The reactions can be represented as follows:—

$$2\,KMnO_4 + 5\,SO_2 + 2\,H_2O = K_2SO_4 + 2\,MnSO_4 + 2\,H_2SO_4$$
$$2\,K_2CrO_4 + 3\,SO_2 + 2\,H_2SO_4 = 2\,K_2SO_4 + Cr_2(SO_4)_3 + 2\,H_2O.$$

The reaction with potassium dichromate can be represented as follows :—

$$K_2Cr_2O_7 + H_2SO_4 + 3\ H_2SO_3 = Cr_2(SO_4)_3 + K_2SO_4 + 4\ H_2O.$$

Action of Sulphur Dioxide on Iodine.—Iodine is reduced to hydriodic acid by sulphur dioxide in the presence of water, but the reaction ceases when a small quantity of hydriodic acid has been produced, owing to the tendency of the latter to reduce sulphuric acid, *i.e.* for the reaction to proceed in the reverse direction. This is an example of a *reversible action*, the exact course of the reaction depending on the *relative masses* of the reacting substances (other conditions remaining the same)—

$$I_2 + 2\ H_2O + SO_2 \rightleftharpoons H_2SO_4 + 2\ HI.$$

If, therefore, the hydriodic acid can be removed, the reaction will proceed from left to right, and is in fact used in the estimation of sulphites.

Exp. 95. Liberate iodine from potassium iodide by adding a *few drops* of chlorine water; now add an aqueous solution of sulphur dioxide, and the brown colour of the iodine will disappear.

311. Additive Compounds of Sulphur Dioxide.—Sulphur dioxide combines with chlorine in bright sunlight or in the presence of acetic acid or of camphor to form sulphuryl chloride, SO_2Cl_2—

$$SO_2 + Cl_2 = SO_2Cl_2.$$

It also combines with certain metallic peroxides to form sulphates—

$$Na_2O_2 + SO_2 = Na_2SO_4.$$

In the case of lead peroxide, PbO_2, the reaction is accompanied with incandescence—

$$PbO_2 + SO_2 = PbSO_4.$$

312. Composition of Sulphur Dioxide.—This may be determined by synthesis. By means of the arrangement shown (Fig. 63), a fragment of sulphur may be burnt in oxygen. The sulphur is contained in a small bone-ash crucible. Two stout copper leads are cemented into the stopper of the bulb,

and the crucible is supported by one of these. A thin piece of platinum wire is so arranged that it is in contact with the two leads and with the sulphur. When the current is passed, this thin wire becomes very hot and ignites the sulphur.

The apparatus and the oxygen used in the experiment must be free from moisture. The gas in the globe at first expands owing to the heat of combustion, and forces the mercury up the further limb, but on cooling it returns to its original volume. It is seen, therefore, that during the combination of sulphur and oxygen to form sulphur dioxide no alteration in volume occurs, that is to say, *sulphur dioxide contains its own volume of oxygen.*

It follows then from Avogadro's hypothesis that one molecule of sulphur dioxide must contain one molecule of oxygen. Further, since the molecular weight of the gas as found from its density is 64, the composition, deduced by a method similar to that used for hydrogen bromide (see § 196), must be represented by the formula SO_2.

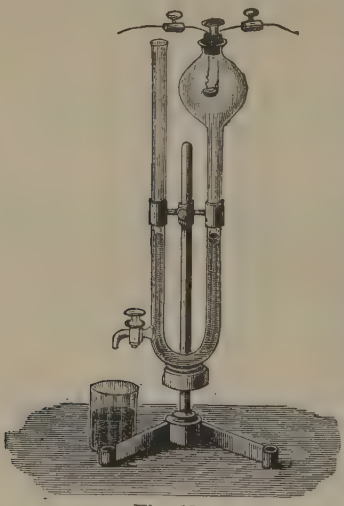


Fig. 63.

313. Sulphurous Acid and Sulphites. — We have seen that sulphur dioxide dissolves readily in water, forming an acid, H_2SO_3. This acid has never been isolated from its dilute aqueous solution, any attempt to concentrate the solution resulting in decomposition with loss of sulphur dioxide. It is a weak acid and a reducing agent, because it readily takes up oxygen to form sulphuric acid.

Sulphurous acid contains two atoms of hydrogen in its molecule, both of which are replaceable by metals; it is,

therefore, a *dibasic* acid (see § 48), and gives rise to two series of salts called *sulphites*. The first series in which both atoms of hydrogen are replaced are the *normal* sulphites, *e.g.* Na_2SO_3, K_2SO_3, $CaSO_3$; the second series in which only one hydrogen atom is replaced are the *acid* sulphites, *e.g.* $NaHSO_3$, $KHSO_3$, $Ca(HSO_3)_2$. $NaHSO_3$ is called by three different names, viz. acid sodium sulphite, sodium hydrogen sulphite, and bisulphite of soda; the second regards sulphurous acid as a hydrogen salt, the third is a popular name which has no scientific basis.

The sulphites of the alkali metals may be prepared by passing sulphur dioxide into solutions of the corresponding hydroxides or carbonates.

Exp. 96. Take 50 c.cm. of a solution of caustic soda, and pass sulphur dioxide into it till it is saturated with the gas. On allowing the solution to evaporate at ordinary temperatures (it decomposes when heated), or on adding alcohol to it, the *acid salt*, sodium hydrogen sulphite, separates out—

$$NaOH + SO_2 = NaHSO_3.$$

If we add a second 50 c.cm. of the same solution of caustic soda we shall then obtain on evaporation or treatment with alcohol the *normal* salt—

$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O.$$

In a similar way, substituting caustic potash for caustic soda, the sulphites of potash may be prepared. The normal sulphites of all metals excepting the alkali metals are insoluble in water, and may be obtained as precipitates by the addition of a soluble salt of the metal to a solution of an alkaline sulphite—

$$CaCl_2 + Na_2SO_3 = CaSO_3 + 2\,NaCl.$$

Sulphites slowly take up oxygen from the air, passing into sulphates, and all sulphites are decomposed by acids with evolution of SO_2.

Calcium bisulphite, $Ca(HSO_3)_2$, is an important salt which is used in the manufacture of paper from wood pulp.

Sulphur Trioxide, SO_3.

314. History and Preparation: (*a*) *History.*—Sulphur trioxide was said to be prepared by Basil Valentine in the fifteenth century, and was called "philosophical salt." Later,

Scheele (1777) called it sulphuric anhydride. Until 1875 sulphur trioxide was usually prepared by distilling Nordhausen acid, but in that year Winkler found that sulphur dioxide and oxygen could be made to combine, using very finely-divided platinum as a catalyst. Winkler's discovery has only been commercially applied in recent years.

Sulphur trioxide occurs in small quantity with the sulphur dioxide formed during the combustion of sulphur or iron pyrites.

(*b*) *Preparation.*—Sulphur dioxide and oxygen are passed over platinised asbestos. The gases must be dry, and the platinised asbestos gently heated, and there then appear at the exit dense white fumes, which if passed into a cool dry receiver condense to white silky needles of sulphur trioxide. This method of preparation is employed in the *Contact Process* for sulphuric acid, and is described more fully in § 325.

A method which was formerly employed in the production of sulphur trixode in large quantities is based on the decomposition of ferrous sulphate, $FeSO_4 \cdot 7\ H_2O$. This body, when heated, first loses most of its water of crystallisation. The partially dehydrated salt more strongly heated is decomposed thus—

$$2\ FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

The water which still remains attached to the salt, however, combines with some of the SO_3 forming H_2SO_4, and this takes up another molecule of SO_3 forming $H_2S_2O_7$—

$$H_2O + SO_3 = H_2SO_4 \text{ and } H_2SO_4 + SO_3 = H_2S_2O_7.$$

The acid thus produced is known as Pyrosulphuric acid, or Nordhausen sulphuric acid, or oleum; it differs from ordinary sulphuric acid, as the molecule contains one molecule more of sulphur trioxide. It fumes when exposed to moist air, and is often termed *fuming sulphuric acid*. Oleum comes into commerce with varying concentrations of excess of SO_3. This liquid, which condenses from the distillation of partially dehydrated ferrous sulphate, when removed from the receiver and heated, yields the SO_3 which it has taken up, leaving behind sulphuric acid—

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

Sodium pyrosulphate on heating to 60° C. yields SO_3—

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

By distilling with a powerful dehydrating agent, such as phosphorus pentoxide, the elements of water may even be removed from sulphuric acid itself—

$$P_2O_5 + H_2SO_4 = 2\,HPO_3 + SO_3.$$

(*c*) *Laboratory Preparation.* — A convenient laboratory method for the preparation of sulphur trioxide is as follows:— Dry sulphur dioxide, conveniently obtained from a siphon, and dry oxygen (from a cylinder) are passed through a tube which contains platinised asbestos, and which is connected to a receiver surrounded by a freezing mixture (Fig. 64).

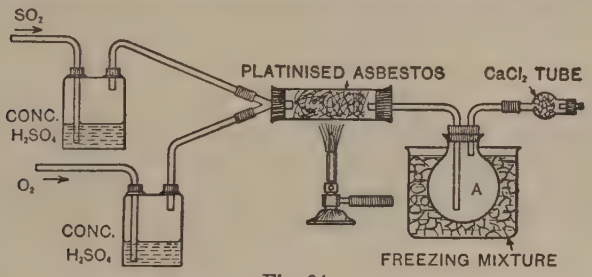


Fig. 64.

The sulphur dioxide and oxygen are dried by passing through concentrated sulphuric acid; and the catalyst is heated during the passage of the gas by a fan burner. The catalyst, platinised asbestos is conveniently made by soaking asbestos wool in a solution of so-called "platinic chloride," H_2PtCl_6 (chloroplatinic acid), then igniting the asbestos as a result of which it is covered with a deposit of finely-divided platinum. Under these conditions sulphur trioxide collects in A.

315. Properties of Sulphur Trioxide.—At ordinary temperatures sulphur trioxide forms white transparent needles, which melt at 17° C.; at a red heat it breaks up into sulphur dioxide and oxygen.

Sulphur trioxide exists in two forms : α sulphur trioxide, which is a liquid boiling at 44·8° C., and melting at 17° C., and β sulphur trioxide, an asbestos-like crystalline solid, which volatilises at 50° C. without melting. The α form is the more chemically active.

Sulphur trioxide combines very eagerly with water, evolving much heat, and in contact with water it gives a hissing sound like that of the quenching of hot iron ; sulphuric acid is thereby formed.

It is of interest to add that sulphur trioxide enters into direct combination with certain metallic oxides, with the production of the corresponding sulphates ; for instance, when baryta, BaO, and sulphur trioxide are mixed they combine to form barium sulphate, $BaSO_4$, and so much heat is evolved that the mass becomes incandescent.

Sulphuric Acid, H_2SO_4.

316. History.—Sulphuric acid was known to Geber about the eighth century ; he apparently obtained it by the distillation of alum. The writings attributed to Basil Valentine (about 1600) mention the preparation of sulphuric acid by distilling green vitriol—the method until quite recently used for "Nordhausen" sulphuric acid—and by burning sulphur with the addition of saltpetre, in the presence of water. The latter method was the one adopted when the acid began to be manufactured on a considerable scale, about the middle of the eighteenth century. The reaction was at first carried out in large glass globes, but these were soon replaced by leaden chambers, which gradually grew in size to the enormous structures of the present day, and were made continuous in their working.

The only difference between the original and the present method is that all the materials are now introduced into the chambers in the gaseous instead of the solid or liquid form : steam is brought in instead of water, sulphur dioxide instead of sulphur, and oxides of nitrogen instead of saltpetre.

The "Contact Process," which will in time probably replace the Chamber Process, was the outcome of a discovery of

Winkler and others in 1875, viz. that sulphur dioxide combined with oxygen to form sulphur trioxide when passed over platinised asbestos. Before 1875 many workers had prepared sulphur trioxide in a similar way, but they did not succeed in finding the conditions for the process on an industrial basis.

Later, Knietsch and others developed the idea of the preparation of sulphur trioxide by catalytic means, and now the process is employed to an extent which grows bigger every year.

317. Manufacture by the Lead Chamber Process.—We have seen that under certain circumstances sulphur dioxide combines with oxygen to form sulphur trioxide, and that this in presence of water gives sulphuric acid. We have also seen that the oxidation of sulphurous acid to sulphuric acid takes place slowly when its aqueous solution is exposed to air at ordinary temperatures.

Such methods are, however, not suitable for the production of large quantities* of sulphuric acid as an article of commerce.

The oxidation of sulphurous acid is effectually performed by the intervention of the oxides of nitrogen, and on the large scale sulphur dioxide, oxygen (supplied in the form of air) and steam are brought together, and these in presence of oxides of nitrogen form sulphuric acid.

The *sulphur dioxide* in works where a very pure acid is made is obtained by burning brimstone, but in the very large majority of cases iron pyrites is used as the source of the gas. This is burnt in a series of "kilns," and the heat arising from the combustion is sufficient to render the operation continuous, fresh charges being added from time to time—

$$2\,FeS_2 + 11\,O = Fe_2O_3 + 4\,SO_2.$$

The *nitric acid* from which the oxides of nitrogen are derived is prepared by the action of concentrated sulphuric acid on Chile saltpetre, $NaNO_3$—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3\,;$$

the acid fumes are carried into the flues along which the sulphur

* Over a million tons of oil of vitriol are produced in Great Britain alone in the course of a year.

dioxide and air pass, and there intermingle with these gases.

The *air* is drawn in through the pyrites burners or kilns, the draught being maintained by means of a chimney, and by adjustment of the doors of the kilns so as to admit the quantity of air which experience has shown to be necessary. The *steam* is supplied from low pressure boilers, and introduced into the " chambers " in such a way as to become intimately associated with the other products.

The reaction ending in the production of sulphuric acid does not take place under the circumstances very rapidly, and it is necessary to provide for a lengthened period of contact between the various bodies which take part in it. The gases are led into a series of large chambers where they meet with the steam. These are usually three in number, and have a total capacity of 100,000 to 150,000 cub. ft., the relation of the sulphur burnt to the capacity of the chamber being such that the average time occupied by the gas in traversing the chambers is something like three hours. The walls and floor of the chambers are constructed of sheet-lead supported on a wooden framework, lead being a metal which is scarcely attacked at all by sulphuric acid of the strength produced in the chambers. The chambers are kept cool enough to serve as condensers, so that the acid collects on the floor, and is drawn off periodically.

318. The Recovery of the Oxides of Nitrogen.—In practice, the higher oxides of nitrogen are carried forward in the chambers, and would escape at the exit. To avoid this waste, advantage is taken of the fact that they are absorbed by *concentrated* sulphuric acid. The exit gases from the chambers are therefore passed through a tower (known as the *Gay-Lussac tower*), packed with coke, down which concentrated sulphuric acid constantly trickles.

In order to render these absorbed gases again available in the production of sulphuric acid, the acid which has traversed the Gay-Lussac tower is pumped up to the top of a *Glover tower* placed at the entrance of the chambers. Some of the more dilute " chamber acid " is also pumped up to the top, and a mixture of the two acids is run down the tower, which

is packed with flints. The nitrated acid is acted upon by the sulphur dioxide which passes up the Glover tower on its way from the pyrites burners to the chambers, with formation of sulphuric acid and evolution of nitric oxide; the latter is carried forward into the chambers along with the other gases. The Glover tower performs the further functions of cooling the gases before they enter the chambers, and of concentrating the weak chamber acid. The acid which escapes from the Glover tower contains about 80 per cent. H_2SO_4.

319. Details Relating to the Sulphuric Acid Plant shown in Fig. 65: (1) *Pyrites Burners.*—These are shown partly in section, so as to indicate the charge and the common flue into which the gas passes. There are 24 burners, a second row of 12 being placed back to back with those shown. The various doors on the front of the burners serve for charging the ore, stirring the charge when necessary, and finally for removing the burnt ore which has fallen into the ashpit underneath.

(2) *The Glover Tower.*—This is packed with flints, through which trickle from the tanks above (*a*) strong nitrated acid, which has been used to absorb nitrous fumes in the Gay-Lussac tower; (*b*) weak chamber acid.

(3) *The Gay-Lussac Tower.*—This is packed with coke, and the strong acid (specific gravity 1·78) which is supplied from the tank above, passes over the coke and absorbs any oxides of nitrogen present in the exit gases from the chambers.

(4) *The Course Taken by the Gases.*—The sulphur dioxide and air (in excess) pass along the common flue AB from the pyrites burners over the nitre-pots, and then along the pipe C, through the Glover tower. At D they pass in at the front of chamber No. 1, and thence from the back at E to the back of chamber No. 2, entering this at F by the pipe EF; similarly by GH from the front of chamber No. 2 to the front of No. 3, and from the back of this to the base of the Gay-Lussac tower by KL. Having traversed the Gay-Lussac tower the exit gas finally passes off to the chimney by the outlet at the upper part of the tower. The steam is blown in at the ends of the chambers in such a way as to travel always in the

PLANT FOR MANUFACTURE OF SULPHURIC ACID. SCALE 18 FT. TO THE INCH.

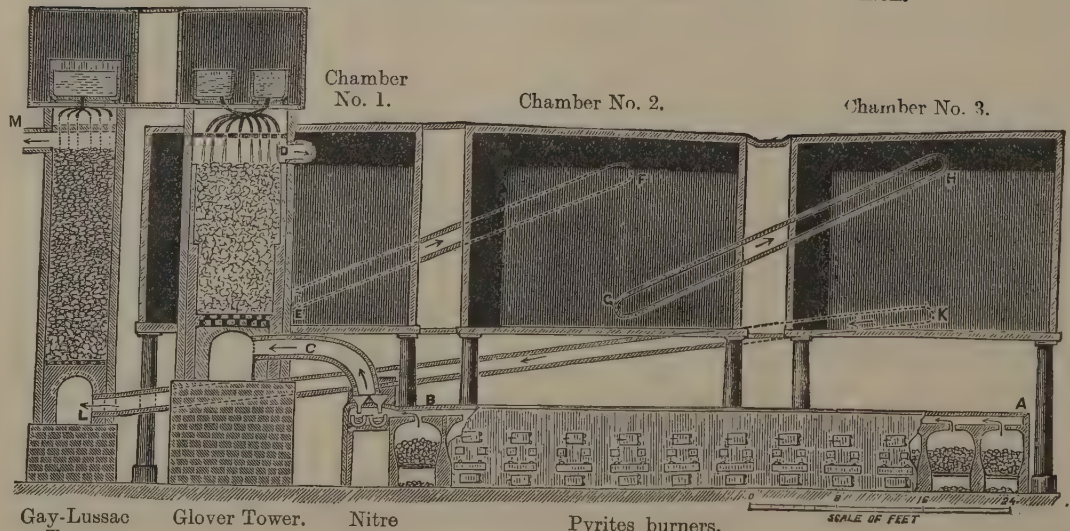


Fig. 65.

direction of the draught, that is to follow the same course as that taken by the gases. Each chamber is 25 ft. wide, 20 ft. high, and 100 ft. long, and they are seen in the figure in transverse section, so that the direction of the length would be perpendicular to the plane of the paper.

The functions of the various parts of the sulphuric acid plant may be summed up thus—

(*a*) *The Chambers* (1) bring about a prolonged contact between the reacting bodies.

(2) Condense the sulphuric acid which collects as the chamber acid (specific gravity 1·6, containing nearly 70 per cent. H_2SO_4) on the floor of the chamber.

(*b*) *The Gay-Lussac Tower* absorbs the oxides of nitrogen in the *exit* gases from the chamber.

(*c*) *The Glover Tower* (1) effects discharge of oxides of nitrogen from the nitrated acid produced in the Gay-Lussac tower.

(2) Assists in the actual production of sulphuric acid.

(3) Cools the gases from the pyrites burners, the heat so absorbed concentrating the acid to specific gravity 1·75 or approximately 80 per cent.

320. Concentration of the Acid.—The acid obtained from the Glover Towers was formerly concentrated up to 77 per cent. sulphuric acid by evaporation in earthenware pans, which easily cracked, and later in leaden pans. Lead is attacked by the hot acid of this strength (approximately), and further concentration is now effected by the following methods :—

(1) Boiling in glass or platinum stills.

(2) *The Cascade System*, in which pans, made of acid-resisting material (fused sand or silica, alloys of iron and silicon such as " tantiron," etc.), and provided with a lip are arranged in series, each one at a level lower than the previous one ; thus the strong acid entering the top pan gets stronger by evaporation as it flows cascade-like to the next pan, and so on. The pans are heated from below. Special hoods of lead are arranged to condense the acid fumes evolved.

(3) *Kessler's Method*, by which very hot gases (products from the combustion of producer-gas) pass over, under, and through the sulphuric acid on the counter-current principle.

(4) *Gaillard Towers* (see § 321).

321. Recent Improvements.—The growth of the Contact Process for the manufacture of sulphuric acid has caused many improvements to be made in the Chamber Process.

The burners have been improved considerably. The nitre pots are being abandoned and nitric acid is run into the Glover Tower. This ensures a more regular flow of oxides of nitrogen. The leaden chambers have been re-designed, so that the gases can have a longer path and complete the reactions. Water in the form of a fine spray instead of steam is introduced into the chambers tangentially, and thus an eddy is set up which gives considerably better mixing of the constituents. The rate of working has been increased by aspirating the gases, using fans. The Gay-Lussac Towers have been re-designed so that more efficient scrubbing of the gases is obtained, and in the second Gay-Lussac Tower the gases are cooled by a lead spiral to 25° C. to give better absorption.

For the concentration of the acid Gaillard Towers are employed. These consist of cylindrical towers built of volvic lava, which is a stone very resistant towards hot concentrated sulphuric acid. Down the tower weak acid is sprayed, and the downward spray meets an upward current of hot gases from the combustion of producer gas. The gases enter at about 1000° C. and leave at about 200° C., and under these conditions a concentrated acid is obtained. To prevent loss as " acid mist " the gases pass out through a coke filter.

322. Impurities in Commercial Sulphuric Acid.—Commercial concentrated sulphuric acid, as prepared by the lead chamber process, may contain several impurities in addition to the 1·5 per cent. of water; the chief are *lead sulphate*, *arsenic*, and the *higher oxides of nitrogen*.

Of these, *lead sulphate* is always present, being produced by the action of the acid on the concentration pans. It may be

detected by diluting the acid when a white cloudiness appears, since lead sulphate is insoluble in dilute sulphuric acid, though soluble in the strong acid.

Arsenic is a frequent impurity and is derived from the pyrites. Its presence may be detected by means of Marsh's test (see *Inorganic Chemistry, Mainly Metals*).

The presence of *oxides of nitrogen* may be detected in the following way :—Shake up vigorously a stoppered bottle half-filled with the acid. Now hold an iodised starch paper* above the acid in the bottle. If it acquires a blue colour, oxides of nitrogen were present in the acid. The explanation is that the higher oxides of nitrogen liberate iodine from potassium iodide and this gives its characteristic blue colour with the starch.

To remove these impurities the following steps are taken :— The acid is diluted, which causes most of the lead sulphate to be precipitated. Arsenic may then be removed, by means of sulphuretted hydrogen. The dilute acid flows down a tower and meets an ascending current of sulphuretted hydrogen. On a smaller scale barium sulphide is added, when barium sulphate is precipitated and the sulphuretted hydrogen thus produced precipitates the arsenic, etc.—

$$BaS + H_2SO_4 = H_2S + BaSO_4$$

$$H_2S + As_2O_3 = As_2S_3 + 3\,H_2O.$$

The acid is then decanted from the insoluble substances.

Another method consists in treating sulphuric acid at 100° C. with dry HCl, the arsenic formed being subsequently volatilised as the trichloride. Oxides of nitrogen are easily eliminated by adding ammonium sulphate when concentrating the acid.

If acid of greater purity is then required, it is distilled from platinum or platinum-gold, from glass, or from fused silica stills. At first weak acid passes over, accompanied by the oxides of nitrogen. When the boiling-point reaches 338° C. the receiver is changed and acid then collects, which is pure, except that it contains 1·5 per cent. of water.

* Made by dipping unglazed paper successively in potassium iodide solution and starch solution, and then drying.

Acid containing 100 per cent. H_2SO_4 cannot be obtained by distillation alone. It is prepared by adding sulphur trioxide to the 98 per cent. acid, and then on freezing, crystals of pure sulphuric acid, melting at 10° C., separate out.

323. Laboratory Representation of the Sulphuric Acid Manufacture.—The formation of sulphuric acid may be represented in the laboratory by taking a large flask (5 litres) and fitting it with a cork provided with five holes through which pass tubes delivering—

(1) Sulphur dioxide (for preparation see § 308),
(2) Nitric oxide („ „ „ § 279),
(3) Steam,
(4) Oxygen from a gasholder;

while the fifth hole is provided with a tube opening into the air. The arrangement is shown in Fig. 66.

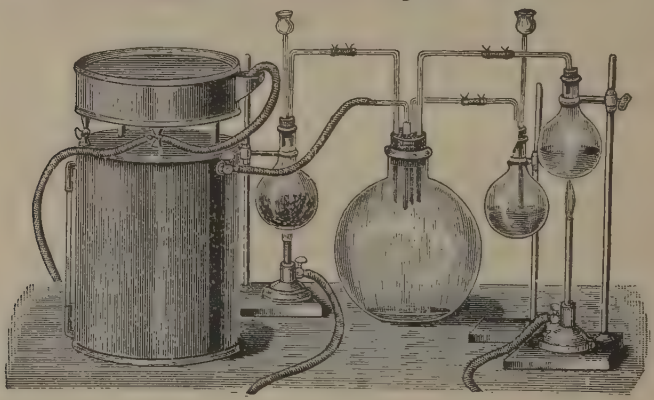


Fig. 66.

Pass some sulphur dioxide, nitric oxide, steam, and oxygen into the flask, then shut off the steam supply; crystals of nitrosulphonic acid (lead chamber crystals) may be seen to form. On clearing the flask of red fumes by a current of oxygen, and then passing in more steam, these crystals will

dissolve with the evolution of red fumes. After allowing the reaction to go on for some minutes, the liquid condensed in the flask may be tested for sulphuric acid (see § 329).

324. The Theory of the Sulphuric Acid Manufacture.—As we have seen (§ 310), sulphur dioxide under the action of air and moisture is transformed into sulphuric acid, but the change takes place very slowly, and the sulphuric acid obtained is extremely dilute. In presence of certain substances, notably the higher oxides of nitrogen as in the sulphuric acid chambers, the conversion is more rapid : but much difference of opinion exists as to the actual changes which take place, and even as to the particular oxides of nitrogen which take part in the reaction.

The first theory was suggested by Clément and Desormes in 1806, and later developed by Davy, as follows :—

$$2\,SO_2 + 3\,NO_2 + H_2O = NO + 2\,SO_2(OH)(ONO).$$
(Chamber Crystals)

The NO is changed into NO_2 by the air, and the crystals (chamber crystals) form H_2SO_4 with air and steam, and NO_2 is regenerated—

$$2\,SO_2(OH)(ONO) + H_2O + O = 2\,H_2SO_4 + 2\,NO_2,$$

and the cycle continues.

Berzelius, however, said that the formation of nitrosulphonic acid is not necessary to the process and does not occur in chambers working normally. He regarded the nitric oxide (NO) as the body which brings about the formation of the sulphuric acid. This it does by taking up oxygen from the air and forming nitrogen peroxide (NO_2), which in its turn oxidises the sulphur dioxide, and in presence of steam forms sulphuric acid, being itself reduced again to nitric oxide, the alternate oxidation and reduction going on indefinitely—

(1) $NO_2 + SO_2 + H_2O = NO + H_2SO_4$.

(2) $2\,NO + O_2 = 2\,NO_2$.

It is however observed that if the chambers are insufficiently supplied with steam, chamber crystals are formed.

A third theory due to Raschig suggests that the intermediate

compound is nitrosisulphonic acid, $SO_2(OH)NO.OH$ and not nitrosulphonic acid—

$$H_2O + NO_2 + SO_2 = SO_2.(OH)NO.OH$$
$$SO_2(OH)NO.OH = H_2SO_4 + NO.$$

The theory more recently proposed by Lunge, on the other hand, assumes nitrogen trioxide to be the true intermediary in the formation of sulphuric acid, and nitrosulphonic acid to be continually formed in the chambers and decomposed again by the excess of steam according to the equations—

$$(3)\ 2\,HNO_3 + 2\,SO_2 + H_2O = 2\,H_2SO_4 + N_2O_3.$$
$$(4)\ N_2O_3 + O_2 + 2\,SO_2 + H_2O = 2\,SO_2(OH)(NO_2).$$
$$(5)\ 2\,SO_2(OH)(NO_2) + H_2O = N_2O_3 + 2\,H_2SO_4.$$

Under some conditions, and especially where the gases are just entering the chambers and sulphur dioxide is in large excess, it is, however, admitted that nitric oxide plays a prominent part. With this exception Lunge's theory is not inconsistent with the observations recorded in actual working on the large scale.

325. "Contact Process" for the Manufacture of Sulphuric Acid.—This process consists essentially in bringing about the combination of sulphur dioxide and oxygen by contact with a catalyst (hence the name "contact process"), and converting the sulphur trioxide so produced into sulphuric acid.

The following is a brief description of the method of procedure :—The gases from pyrites burners such as those employed in the older process are very carefully purified, so that they contain nothing but sulphur dioxide, oxygen, and nitrogen. This purification is necessary because the catalyst is easily "poisoned," *i.e.* rendered inoperative by impurities in the gases.

The purification process involves three stages. The gases are passed through the "dust chamber" in which steam is injected. They are then cooled to about 100° C. by passage through leaden pipes and go on to be "scrubbed" through towers down which water is sprinkled. The gases are finally

dried by passage through a tower where they meet a descending stream of concentrated sulphuric acid.

The gases are next heated up to the temperature at which sulphur dioxide and oxygen combine in contact with platinised asbestos. They are then passed up an iron cylinder containing a number of vertical iron pipes.

These pipes are packed with platinised asbestos and the gases pass *up outside* them, and are then led *down through* them. The reason for this is as follows :—The combination of sulphur dioxide and oxygen which takes place in the pipes is attended with the evolution of a large quantity of heat—

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3 + 45{,}200 \text{ cal.}$$

Now this combination is most complete between certain limits of temperature, viz. 400° — 450° C. The heat developed during the reaction would raise the temperature above the upper limit, were it not for the cooling effect of the current of gas passing up outside the pipes, as in the arrangement shown in Fig. 67.

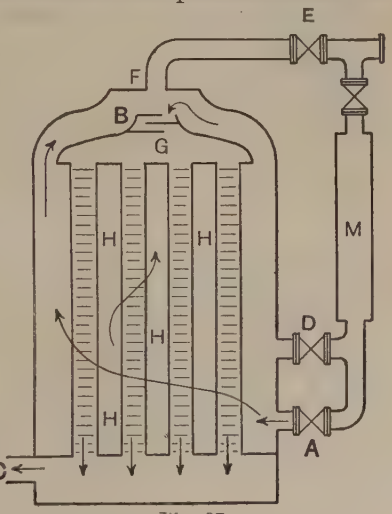


Fig. 67.

326. Practical Details.—The purified gases are heated in M (Fig. 67) and pass through A into the contact chamber. The gases pass up the chamber around the tubes H in a zigzag manner and enter through B. They descend through the tubes H which are packed loosely with platinised asbestos, and escape through C. If the temperature rises too high, cool gases can be admitted through the valves E and D.

A modification of the previous process is as follows :—The gaseous mixture passes through A (Fig. 68) and is heated by passage over the hot pipes B. The gases pass up the apparatus and enter D to descend through the catalytic mass and escape by means of B through C.

The products escaping from C are passed through 98 per cent. sulphuric acid, which completely removes the sulphur trioxide. It is found that acid of this strength absorbs sulphur trioxide very much more readily than either water or dilute acid. In order to keep the strength of the absorbing acid at 98 per cent., water or dilute acid is continuously added, the excess of concentrated acid being drawn off. The whole of the sulphur trioxide is thus converted into strong sulphuric acid.

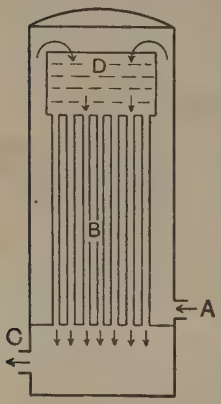


Fig. 68.

A large quantity of *fuming sulphuric acid* is manufactured by the contact process. It is obtained by absorbing the sulphur trioxide from the pipes in strong sulphuric acid, no water being added as when ordinary sulphuric acid is required. Since, however, under these conditions the absorption is not complete, the gas is finally passed through acid, the strength of which is maintained at 98 per cent., as described above. This removes the remainder of the sulphur trioxide.

327. Properties of Sulphuric Acid.—The pure concentrated acid is a thick oily liquid (specific gravity 1·84), from whence it derives the name, *oil* of vitriol. It boils at 338° C., with partial decomposition, so that when the acid containing 100 per cent. H_2SO_4 is distilled the residue becomes weaker, until it reaches a strength of about 98·5 per cent. H_2SO_4, at which it remains constant. *Pure* sulphuric acid is a very poor conductor of electricity.

It is highly corrosive, charring wood, sugar, and other organic substances even at the ordinary temperature. This is

largely owing to the great avidity with which it takes up water. Wood consists mainly of cellulose, a compound of carbon, hydrogen, and oxygen in the proportions in which they are contained in water: the acid therefore abstracts water, leaving a mass of carbon. The reaction with sugar may be represented by—

$$\underset{(H_2SO_4)}{C_{12}H_{22}O_{11}} = 12\,C + 11\,H_2O.$$

The methods of preparation of two common gases, ethylene and carbon monoxide, depend upon this same property (see §§ 412, 452), as does also the employment of concentrated sulphuric acid for drying gases. When sulphuric acid and water are mixed a large amount of heat is evolved again, showing the great affinity they possess for one another, and at the same time there is a considerable diminution in volume.

Two hydrates of sulphuric acid have been isolated, $H_2SO_4.H_2O$ (*i.e.* $SO_3.2\,H_2O$) called *sulphuric acid monohydrate* and $H_2SO_4.4\,H_2O$ (*i.e.* $SO_3.5\,H_2O$) called *sulphuric acid tetrahydrate.*

When sulphuric acid vapour is heated to a temperature of about 450° C. it is almost completely dissociated into water and sulphur trioxide; this is shown by the fact that the vapour density is only half what it should be if the molecules consisted of H_2SO_4.

The following considerations will show that the low value of the vapour density proves that dissociation has taken place. Since each molecule of sulphuric acid gives two molecules on dissociation, one of H_2O and one of SO_3, it follows from Avogadro's hypothesis that the volume of the dissociation products will be double the volume of the sulphuric acid from which they are derived (on reduction to standard conditions). Consequently the vapour density will be half the theoretical value, which agrees with the experimental result stated above.

The vapour density of sulphuric acid is said to be *abnormal* on account of its value being less than the theoretical number; we shall return to this subject of abnormal vapour density in § 346.

When the mixture of water and sulphur trioxide obtained by heating sulphuric acid vapour has its temperature still further raised the sulphur trioxide breaks up into sulphur dioxide and oxygen. Thus, when sulphuric acid is dropped on red-hot bricks it decomposes, as represented in the following equation—

$$2\,H_2SO_4 = 2\,H_2O + 2\,SO_2 + O_2.$$

This fact has been utilised as a means of manufacturing oxygen from sulphuric acid on the large scale. Some of its salts also decompose in a similar way when heated, *e.g.*—

$$2\,Fe_2(SO_4)_3 \underset{\text{(above 800° C.)}}{=} 2\,Fe_2O_3 + 6\,SO_2 + 3\,O_2.$$

Sulphuric acid is an oxidising agent, though a much weaker one than nitric acid, as we should expect from the smaller percentage of oxygen it contains and the very much higher temperature required to break it up with separation of free oxygen. Thus it is only when *hot and concentrated* that sulphuric acid exhibits oxidising properties. We have already (§ 308) met with examples of the oxidation of both metals (copper and mercury) and non-metals (carbon and sulphur) by sulphuric acid ; most of the remaining metals and some other non-metals are also oxidised by the hot strong acid.

328. Action of Sulphuric Acid on Metals.—*Dilute* sulphuric acid dissolves some metals, such as zinc, iron, and magnesium, with formation of a sulphate of the metal and hydrogen.

Concentrated sulphuric acid has practically no action on common metals in the cold, a few bubbles only of hydrogen being produced. When warmed, however, it reacts with most metals, producing sulphates of the metals and sulphur dioxide mixed with hydrogen ; in the cases of copper and nickel some subsulphide is produced at the same time. As a type of the reaction which takes place between a metal and strong sulphuric acid, we may write the equation which expresses the main result of the interaction of copper and sulphuric acid, viz.—

$$Cu + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + SO_2.$$

As regards the actual *modus operandi* of the reaction two

explanations have been advanced. The first suggests that the primary reaction is the formation of a sulphate of the metal and hydrogen. The hydrogen being in the nascent state, oxidises itself at the expense of the oxygen of the sulphuric acid, forming water and sulphur dioxide thus—

$$\begin{cases} Cu + H_2SO_4 = CuSO_4 + 2\,H, \\ 2\,H + H_2SO_4 = SO_2 + 2\,H_2O. \end{cases}$$

(H: Nascent.)

The second explanation suggests that the primary action is the oxidation of the metal by the acid, and that this is followed by solution of the oxide in an excess of acid. Thus—

$$\begin{cases} Cu + H_2SO_4 = CuO + H_2O + SO_2, \\ CuO + H_2SO_4 = CuSO_4 + H_2O. \end{cases}$$

In the following table a *résumé* of the action of sulphuric acid on the common metals is given; the gaseous products are not mentioned because, in all cases, with *cold dilute* acid hydrogen is evolved, and with *hot concentrated* acid sulphur dioxide (with some hydrogen).

ACTION OF SULPHURIC ACID ON METALS.

Metal.	Products with Cold Dil. H_2SO_4.	Products with Hot Conc. H_2SO_4.
Magnesium ...	$MgSO_4$	$MgSO_4$
Zinc	$ZnSO_4$	$ZnSO_4$
Iron	$FeSO_4$	$Fe_2(SO_4)_3$ and $FeSO_4$
Cadmium	$CdSO_4$	$CdSO_4$
Mercury ...	No action	Hg_2SO_4 (Hg in excess) $HgSO_4$ (H_2SO_4 in excess)
Lead	No action	$PbSO_4$ (action slow)
Copper ...	No action in absence of air	$CuSO_4$ and Cu_2S
Tin	No action	$SnSO_4$
Silver	No action	Ag_2SO_4
Aluminium ...	$Al_2(SO_4)_3$ (action slow)	$Al_2(SO_4)_3$
Bismuth ...	No action	$Bi_2(SO_4)_3$
Nickel	$NiSO_4$ (action slow)	$NiSO_4$ and NiS
Antimony ...	No action	$Sb_2(SO_4)_3$
Gold	No action	No action
Platinum ...	No action	No action

329. The Sulphates.—These are the salts produced by the replacement of the hydrogen in sulphuric acid by metals. They are produced by the action of sulphuric acid on the metals (in some cases), or on metallic oxides, hydroxides, or carbonates. They may also be prepared by evaporating the salts of the more volatile acids, such as hydrochloric and nitric acids, to dryness with sulphuric acid ; the more volatile acid is driven off and a sulphate of the metal is formed.

Three crystalline sulphates which have long been known, *i.e.* ferrous sulphate, $FeSO_4 \cdot 7\ H_2O$, copper sulphate, $CuSO_4 \cdot 5\ H_2O$, and zinc sulphate, $ZnSO_4 \cdot 7\ H_2O$, were called respectively green, blue, and white *vitriol*, from their colours and the glassy transparency of their crystals (L. *vitreum*, glass). Sulphuric acid was originally called *oil of vitriol*, because it was obtained by the distillation of green vitriol.

The sulphates are remarkable for their tendency to form well-defined crystalline double sulphates, *e.g.* alum, $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24\ H_2O$. These compounds are dealt with under the alums and isomorphism (*Inorganic Chemistry, Mainly Metals*).

Insoluble sulphates may be obtained by mixing a solution of a soluble salt of the metal whose sulphate is required with a solution of a soluble sulphate, when double decomposition takes place with precipitation of the insoluble salt. The sulphates of lead, calcium, barium, and strontium are insoluble or only slightly soluble in water, the rest being readily soluble.

Sulphuric acid, like sulphurous acid, is a dibasic acid and forms two classes of sulphates, the *normal* sulphates such as Na_2SO_4, $CaSO_4$, and the *acid* sulphates such as $NaHSO_4$, either one or the other being formed according to whether the base or the acid is in excess.

Test for Sulphates.—The test for sulphates is as follows :—

Exp. 97. Add barium chloride to a solution which contains either sulphuric acid or a sulphate in presence of hydrochloric acid : a white precipitate is formed consisting of sulphate of barium. This is the only common barium salt which is insoluble in water and acids, and the formation of the precipitate is therefore characteristic, and may be taken as a sure indication of the presence of sulphuric acid either in the free state or in combination.

330. Uses of Sulphuric Acid.—Sulphuric acid is the most important of all the acids. It is very largely used in the manufacture of other acids, such as nitric and hydrochloric acids, in the manufacture of salt-cake—the first stage in the Leblanc process for the manufacture of washing-soda—and in the conversion of normal calcium phosphate, $Ca_3(PO_4)_2$, into the acid calcium phosphate, $CaH_4(PO_4)_2$; the latter is much used for agricultural purposes as a fertiliser, because it is soluble in water, whereas the normal salt is insoluble and so cannot be assimilated by plants. As already mentioned, sulphuric acid is used in the laboratory for drying gases and for the preparation of such gases as carbon monoxide and ethylene. It is also largely employed in making *storage cells* or *accumulators* for the generation of electric currents. Sulphuric acid is used extensively in the preparation of explosives and dye stuffs.

331. Sulphur Heptoxide, S_2O_7.—In 1877 Berthelot discovered that on passing electric sparks through a mixture of sulphur dioxide and oxygen, or of sulphur trioxide and oxygen for some time, oily drops of sulphur heptoxide were formed—

$$4\,SO_2 + 3\,O_2 = 2\,S_2O_7.$$

The liquid solidifies to a white crystalline solid which melts at 0° C. and dissolves in water with a hissing sound to form per*di*sulphuric acid (see § 336)—

$$S_2O_7 + H_2O = H_2S_2O_8.$$

332. Sulphur Sesquioxide, S_2O_3.—This is formed as a blue compound when sulphur is added to liquid sulphur trioxide. It readily decomposes into sulphur dioxide and sulphur. With water a violent reaction occurs, and sulphuric acid, polythionic acids, and sulphur are the main products.

Thiosulphuric Acid, $H_2S_2O_3$.

333. Thiosulphuric Acid.—Thiosulphuric acid has not been isolated. A dilute solution is probably obtained by the action of a mineral acid on a thiosulphate, but it is very unstable, undergoing decomposition according to the equation—

$$H_2S_2O_3 = H_2O + SO_2 + S.$$

The *thiosulphates* may be obtained by boiling solutions of sulphites with sulphur when direct combination takes place—

$$\underset{\text{Sodium sulphite.}}{Na_2SO_3} + S = \underset{\text{Sodium thiosulphate.}}{Na_2S_2O_3}.$$

The sodium salt is the most important; it is generally incorrectly called "hyposulphite of soda" or merely "hypo." It is much used in photography on account of the power it possesses of dissolving the haloid salts of silver, a soluble double thiosulphate of silver and sodium being formed—

$$AgCl + Na_2S_2O_3 = NaCl + \underset{\text{Sodium silver thiosulphate.}}{AgNaS_2O_3}.$$

Sodium thiosulphate is also used to remove the last traces of chlorine from a fabric which has been bleached, such a substance being termed an *anti-chlor*. This action depends upon the ease with which it is oxidised to sodium sulphate—

$$Na_2S_2O_3 + H_2O + Cl_2 = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + 2\,HCl + S.$$

Sodium thiosulphate is employed in volumetric analysis for the estimation of iodine—

$$2\,Na_2S_2O_3 + I_2 = 2\,NaI + \underset{\text{Sodium tetrathionate.}}{Na_2S_4O_6}.$$

Test for Thiosulphates.—Thiosulphates in solution are distinguished from sulphites by the fact that with dilute mineral acids they give off sulphur dioxide and also *form a precipitate of finely-divided sulphur*—

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + SO_2 + S + H_2O.$$

334. Hydrosulphurous Acid.—$H_2S_2O_4$ has not been isolated, but a dilute solution is obtained by the action of oxalic acid on sodium hydrosulphite—

$$Na_2S_2O_4 + \begin{matrix}COOH\\|\\COOH\end{matrix} = \begin{matrix}COONa\\|\\COONa\end{matrix} + H_2S_2O_4.$$

It readily decomposes to sulphurous acid and sulphur. The sodium salt, $Na_2S_2O_4$, sodium hydrosulphite, is an important commercial product, and is used extensively in dyeing.

The Persulphuric Acids.

The persulphuric acids can be considered to be derivatives of hydrogen peroxide—

O—H | O—H	O—SO_2·OH | O—H	O—SO_2·OH | O—SO_2OH
Hydrogen peroxide.	Permonsulphuric acid (or Caro's acid).	Perd sulphuric acid (or Marshall's acid).

335. Permonosulphuric Acid or Caro's Acid. H_2SO_5.—Permonosulphuric acid, H_2SO_5, was discovered by Caro in 1898, He made it by the action of concentrated sulphuric acid on potassium persulphate.

It can also be prepared readily by the following methods :—

(1) $\underset{\text{Chlorsulphonic acid.}}{ClSO_3H} + H_2O_2 = H_2SO_5 + HCl$

(2) $SO_3 + H_2O_2 = H_2SO_5$.

Caro's acid is a white crystalline compound, fairly stable and melting at 45° C. It is a very powerful oxidising agent, liberating iodine from potassium iodide, and precipitating peroxides from salts of silver, copper, manganese, etc. It is a monobasic acid.

336. Perdisulphuric Acid or Marshall's Acid, $H_2S_2O_8$.—This is usually called persulphuric acid. The pure acid may be obtained by the action of anhydrous hydrogen peroxide on chlorsulphonic acid—

$$2\,ClSO_3H + H_2O_2 = H_2S_2O_8 + 2\,HCl.$$

It is also produced when sulphuric acid is electrolysed with a high current density, at a temperature of 5° C.-10° C.—

$$\left.\begin{matrix}H_2SO_4\\H_2SO_4\end{matrix}\right\} = \begin{matrix}HSO_4\\|\\HSO_4\end{matrix} + H_2$$

Persulphuric acid is a crystalline solid melting at 65° C. It is a strong oxidising agent in aqueous solution.

337. The Persulphates.—The persulphates can be prepared generally by substituting the corresponding acid sulphate for sulphuric acid in the electrolytic process mentioned above.

(*a*) *Ammonium Persulphate*, $(NH_4)_2S_2O_8$, is used technically in organic chemistry, as a bleaching agent, and in the photographic industry.

(*b*) *Potassium Persulphate*, $K_2S_2O_8$, prepared by the electrolysis of a saturated solution of potassium sulphate in sulphuric acid, is a crystalline substance *only sparingly soluble in water*.

The persulphates are stable salts, but in aqueous solution, or on heating, readily decompose—

$$2\,K_2S_2O_8 = 2\,K_2S_2O_7 + O_2.$$

They are oxidising agents, liberating iodine from potassium iodide and oxidising ferrous salts to ferric salts. Silver salts appear to have a catalytic effect on the oxidising properties of persulphates. Thus potassium persulphate precipitates manganese peroxide from solution of manganese salts, but if silver nitrate is present, a pink solution of potassium permanganate is formed. Unlike barium sulphate, *barium persulphate* is soluble in water.

The Thionic Acids.

338. The Thionic Acids.—The thionic acids are closely related to sulphurous acid and to thiosulphuric acid. They have the general formula—

$$H_2S_xO_6, \quad \text{where} \quad x = 2, 3, 4, 5, 6.$$

The acids have not been isolated. Dilute solutions have been prepared, and on heating break down into a mixture of sulphuric and sulphurous acids and sulphur. The properties of dilute solutions of the acids, and of their salts have been investigated. It is worthy of note that the barium salts of these acids are *soluble* in water.

Compounds of Sulphur with Oxygen and Chlorine.

339. The Three Compounds.—Sulphur forms three compounds with oxygen and chlorine, namely, thionyl chloride, $SOCl_2$, sulphuryl chloride, SO_2Cl_2, and disulphuryl chloride,

$S_2O_5Cl_2$. We shall consider only the first two of these bodies, the last being comparatively unimportant.

340. Thionyl Chloride, $SOCl_2$.—Chlorine monoxide, Cl_2O, combines directly with sulphur (dissolved in chloride of sulphur), forming $SOCl_2$, which is also formed by the action of dry sulphur dioxide on PCl_5—

$$SO_2 + PCl_5 = SOCl_2 + POCl_3.$$

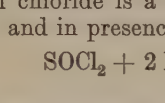
It is also prepared by the action of sulphur trioxide on sulphur dichloride—

$$SO_3 + SCl_2 = SOCl_2 + SO_2.$$

Thionyl chloride is a colourless fuming liquid which boils at 79° C., and in presence of water is decomposed thus—

$$SOCl_2 + 2\,H_2O = H_2SO_3 + 2\,HCl.$$

341. Constitution of Sulphurous Acid.—There are two possible constitutional formulae which may be assigned to sulphurous acid according as we make sulphur tetravalent or hexavalent. They are



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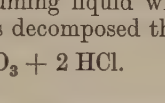
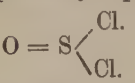
and



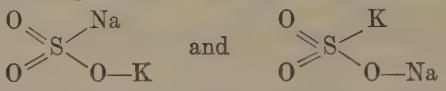
II

Formula I agrees with the fact that sulphurous acid is dibasic (for it is a rule of frequent application that the basicity of an oxyacid depends on the number of hydroxyl groups present in the molecule—the replaceable hydrogen atoms being those of the hydroxyl groups). It also agrees with the formation of sulphurous acid by the action of water on thionyl chloride, which is most probably represented by the formula



On the other hand the salt, potassium sodium sulphite, $KNaSO_3$, is produced in two ways: (1) by the action of NaOH on $KHSO_3$ and (2) by the action of KOH on $NaHSO_3$.

These reactions cannot be accounted for by Formula I, but if Formula II is adopted the salt *may be* represented thus :—



It follows that the *salts* of sulphurous acid are derived from Formula II. The acid itself is most probably an equilibrium mixture of I and II.

342. Sulphuryl Chloride, SO_2Cl_2.—This body is obtained by the direct combination of sulphur dioxide and chlorine in sunlight, or in the presence of acetic acid or camphor as a catalyst. It may also be obtained by heating chlorsulphonic acid, SO_3HCl, in a sealed tube to 200° C.—

$$2\,SO_3HCl = \underset{\substack{\text{Sulphuryl}\\\text{chloride}}}{SO_2Cl_2} + H_2SO_4.$$

A third method consists in acting on concentrated sulphuric with phosphorus pentachloride—

$$H_2SO_4 + 2\,PCl_5 = SO_2Cl_2 + 2\,POCl_3 + 2\,HCl.$$

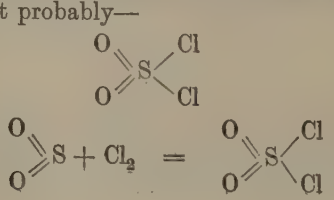
It is a fuming liquid which boils at 70° C. and readily decomposes when brought into contact with water—

$$SO_2Cl_2 + 2\,H_2O = 2\,HCl + H_2SO_4.$$

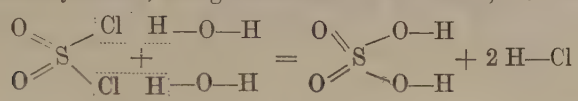
Sulphuryl chloride is, therefore, the acid chloride of sulphuric acid.

343. Constitution of Sulphuric Acid.—We can arrive at the constitutional formula of sulphuric acid in the following manner :—

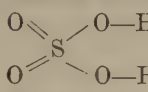
Since sulphuryl chloride is produced by the direct combination of sulphur dioxide and chlorine, its constitutional formula is most probably—



Rewriting the equation for the decomposition of sulphuryl chloride by water, using constitutional formulae, we have—



i.e. the constitutional formula for sulphuric acid is—



This represents it as a dibasic acid, since it contains two hydroxyl groups.

Chlorosulphonic Acid, SO_3HCl.

344. Chlorosulphonic Acid, SO_3HCl.—This interesting body is obtained by direct combination of dry hydrochloric acid gas and sulphur trioxide, or by the action of phosphorus pentachloride, PCl_5, on sulphuric acid—

$$SO_3 + HCl = SO_3HCl$$

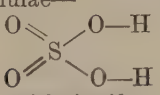
$$H_2SO_4 + PCl_5 = SO_3HCl + POCl_3 + HCl.$$

The first method of production may be conveniently carried out by passing dry hydrochloric acid gas into Nordhausen sulphuric acid; the chlorsulphonic acid boils at 153° C., and may be readily separated by distillation.

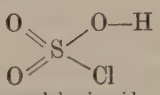
Like SO_2Cl_2 it decomposes in the presence of water, the chlorine atom being replaced by a hydroxyl group with formation of sulphuric acid—

$$SO_3HCl + H_2O = H_2SO_4 + HCl.$$

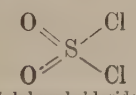
Now chlorosulphonic acid is a monobasic acid, *i.e.* it contains one hydroxyl group; its composition must, therefore, be intermediate between that of sulphuric acid and that of sulphuryl chloride, as shown in the following constitutional formulae—



Sulphuric acid.



Chlorosulphonic acid.



Sulphuryl chloride.

We may now rewrite the equations for the action of phosphorus pentachloride on sulphuric acid, and of water on chlorsulphonic acid in the following manner, using constitutional formulae which are not quite so detailed as those previously used, but have the advantage of being less cumbersome—

$$SO_2(OH)_2 + PCl_5 = SO_2(OH)Cl + POCl_3 + HCl$$

$$SO_2(OH)Cl + H_2O = SO_2(OH)_2 + HCl$$

The equation for the decomposition of chlorosulphonic acid on heating given in § 342 is better written—

$$2\,SO_2(OH)Cl = SO_2(OH)_2 + SO_2Cl_2$$

Chlorosulphonates of the alkali metals are formed by the direct union of SO_3 and a chloride, or by the action of chlorosulphonic acid on a chloride—

$$KCl + SO_3 = SO_2(OK)Cl$$

$$KCl + SO_2(OH)Cl = SO_2(OK)Cl + HCl$$

Selenium and Tellurium.

345. Tellurium, although recognised in 1782 by Muller von Reichenstein as an element, was named Tellurium (from the Latin *tellus* = the earth) by Klaproth in 1798. Berzelius, in 1817, discovered and named Selenium (from the Greek *selēnē* = the moon) because it resembled tellurium, which was discovered a few years earlier.

Selenium and tellurium are rare elements. Selenium occurs with iron pyrites in a few localities, and is thus found in the

" flue dust " of the pyrites burners used in the manufacture of sulphuric acid. It was discovered by Berzelius in " flue dust." Tellurium occurs with gold, silver, and bismuth. These two elements are usually classed as non-metals.

Selenium is a red amorphous body which, like sulphur, exists in several allotropic modifications, whilst tellurium has a gray metallic appearance. Selenium exists in a metallic form, and can be obtained as such by heating any of the allotropic forms at a temperature below its melting point, 217° C. This metallic selenium is a conductor of electricity, whereas the other forms are poor conductors. Further, the electrical resistance is diminished by the action of light, a fact which is used in photometry, in buoys, etc.

Both elements form gaseous compounds, H_2Se, H_2Te, corresponding to sulphuretted hydrogen. They are prepared by a similar reaction, and precipitate selenides and tellurides from solutions of the salts of most metals.

They likewise burn in air forming dioxides, SeO_2, TeO_2, and tellurium on further oxidation yields a trioxide, TeO_3. The dioxides dissolve in water forming acids corresponding to sulphurous acid, which on oxidation give selenic acid, H_2SeO_4, and telluric acid, H_2TeO_4, which form salts like the sulphates.

They unite directly with the halogens to form Se_2Cl_2, $SeCl_4$, Se_2Br_2, $TeCl_4$, $TeBr_2$, etc.

346. Abnormal Vapour Density.—When a volatile compound has a vapour density which has less than the theoretical value calculated from its formula, its vapour density is said to be *abnormal.* We have already discussed one case of this phenomenon in § 327, viz. sulphuric acid, and it was explained that the abnormality is due to the *dissociation* of the acid into sulphur trioxide and water. A similar explanation may be given in other cases, amongst which may be mentioned *ammonium chloride* and *phosphorus pentachloride.*

In the case of ammonium chloride (NH_4Cl) the products of dissociation are ammonia (NH_3) and hydrogen chloride (HCl). That dissociation has actually taken place is proved by the fact that the products may be partially separated by allowing them to diffuse through a porous partition. Ammonia having

the lower density diffuses the more rapidly, and so the vapour which passes through the partition acquires an alkaline reaction, whilst that remaining behind becomes acid to litmus. It should be mentioned that if ammonium chloride is *absolutely dry* its vapour density is normal, *i.e.* it does not undergo dissociation.

In the case of phosphorus pentachloride (PCl_5) the dissociation products are phosphorus trichloride (PCl_3) and chlorine (Cl_2); the presence of the latter is rendered evident by the yellow colour of the vapour.

It should be observed that the term *abnormal vapour density* is really a misnomer. Such cases as we have been discussing were at one time regarded as being *exceptions* to Avogadro's Law, whereas in the light of the explanations given they actually afford a *confirmation* of the Law.

QUESTIONS.—CHAPTER XX.

1. Describe how sulphur dioxide is prepared on the laboratory scale and how it is collected.

2. State the *physical* and *chemical* properties of sulphur dioxide.

3. Explain the bleaching action of sulphur dioxide, and show in what respects it differs from that of chlorine.

4. What is the effect of passing chlorine into a solution of sulphur dioxide in water? Give the equation.

5. Express by equations the action of sulphur dioxide on solutions of (1) ferric sulphate, (2) potassium permanganate in the presence of sulphuric acid, (3) potassium chromate in the presence of sulphuric acid.

6. A little chlorine is passed into a solution of potassium iodide, and then afterwards sulphur dioxide is passed in; state the changes which take place and give equations representing them.

7. "Sulphur dioxide contains its own volume of oxygen." Explain the meaning of this statement, and show how you would prove the truth of it by experiment.

8. Describe the preparation of the normal and acid sulphites of soda; what is the action of sulphuric acid on them?

9. Under what circumstances does sulphur dioxide combine directly with oxygen?

10. How may sulphur trioxide be obtained from (*a*) Nordhausen sulphuric acid; (*b*) ordinary sulphuric acid?

11. Describe the manufacture of sulphuric acid by the "Chamber Process."

12. Discuss the theories suggested to account for the formation of sulphuric acid by the "Chamber Process."

13. Describe the "Contact Process" for the manufacture of sulphuric acid.

14. Discuss the action of heat on sulphuric acid.

15. Compare the reactions between the metals, zinc, mercury, and iron respectively, and (1) dilute sulphuric acid, (2) hot concentrated sulphuric acid.

16. Write down the formulae of the normal sulphates of copper, potassium, lead, iron, and aluminium.

17. What are the chief uses of sulphuric acid?

18. What is the correct name for "hyposulphite of soda"? How is this substance prepared, and what are its properties and uses?

19. Give two methods by which thionyl chloride may be obtained. What is the action of water on this substance?

20. Discuss the constitution of sulphurous and sulphuric acids.

CHAPTER XXI.

PHOSPHORUS.

347. History.—This element was discovered in 1674 by a Hamburg physician named Brand, who prepared it by distilling with sand a mixture of the syrupy residue obtained by evaporation of urine. At that time the name phosphorus was used for substances that appeared luminous in the dark, *e.g.* barium sulphide. The word phosphorus (Greek, *phos*, light, and *phero*, I carry) was then given to Brand's product.

Boyle independently discovered the same process a few years afterwards. In 1771 the presence of phosphorus in bones was shown by Gahn. The preparation of phosphorus from bone-ash was first described by Scheele in 1772, but his process has been considerably modified. Lavoisier, in 1772, first proved that phosphorus is an element, and he investigated some of its compounds. The manufacture of phosphorus on a large scale dates only from the invention of lucifer matches early in the nineteenth century.

348. Occurrence. — Phosphate of lime, $Ca_3(PO_4)_2$, the principal source of phosphorus, forms the essential constituent of the mineral apatite, and of bone-ash. The former occurs in the older formations of the earth's crust as—

Chlorapatite, $3\,Ca_3(PO_4)_2 \cdot CaCl_2$;

and Fluorapatite, $3\,Ca_3(PO_4)_2 \cdot CaF_2$.

Bone-ash is obtained by the dry distillation of bones.

In small quantities phosphates are very widely distributed; all fertile soils contain a small percentage, and they are always found in plants, being, like nitrogen, essential to plant-life.

349. Manufacture of Phosphorus from Bone-ash (Retort Process).—The first step in the manufacture of phosphorus from bone-ash, which is essentially impure calcium phosphate, $Ca_3(PO_4)_2$, consists in treating it with sulphuric acid, when the following reaction takes place :—

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 = 3\ CaSO_4 + 2\ H_3PO_4.$$

When the decomposition is complete, the product is filtered through cinders ; the calcium sulphate remains on the filter, and the phosphoric acid passes through.

The liquid is then concentrated, mixed with charcoal, and further heated almost to dryness, the H_3PO_4 losing water and being converted into HPO_3—

$$H_3PO_4 = HPO_3 + H_2O.$$

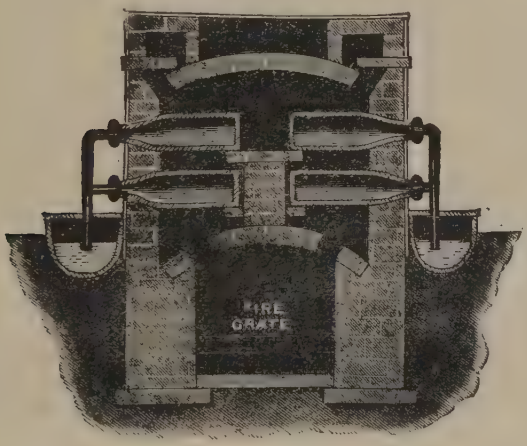


Fig. 69.

Finally, the granular product is heated to full redness in clay retorts placed horizontally in series over a fire (Fig. 69), when the following reaction takes place :—

$$2\ HPO_3 + 6\ C = H_2 + 6\ CO + 2\ P.$$

Luted into the mouth of each retort is an iron pipe, bent at right angles and dipping into water ; the vapour of phos-

phorus is thus led into the water, and there condensed out of contact with air. The temperature of the water is high enough to keep the phosphorus in the liquid state, and it can be run off or ladled out from time to time. It is further refined by re-melting in water, and filtering through chamois leather or canvas to remove suspended matter, and then finally cast into sticks. The details of the purification are, however, a trade secret.

350. Electrical Process.—The manufacture of phosphorus from bone ash by the retort process was, until recent years, the only commercial method of preparation. The electrical process for the manufacture of phosphorus is really the result of an observation of Wöhler. He found that by mixing the bone-ash with sand a better yield of phosphorus was obtained. However, the process was then commercially impracticable because a very high temperature was required, and the calcium silicate formed attacked the retorts. With the use of an electric furnace Wöhler's method was made practicable by Readman, Parker, and Robinson in 1898.

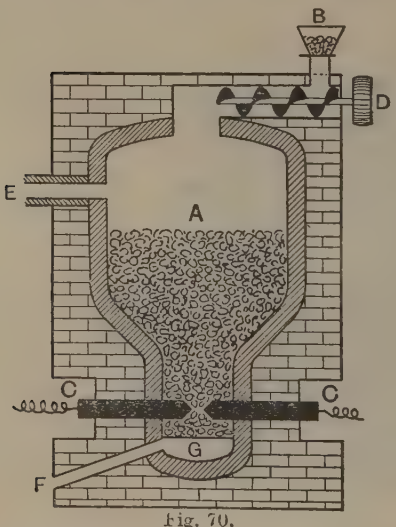


Fig. 70.

The details of the process are as follows:—A mixture of mineral phosphate or of bone-ash, finely divided sand and coke, is heated in an electric furnace (Fig. 70). The mixture, A, is heated by means of thin carbon electrodes (not shown), and when the furnace is hot these are withdrawn and the current

is sent through the carbon electrodes CC. The electric current *raises the temperature* of the mass, and the following reactions may be said to take place :—

$$Ca_3(PO_4)_2 + 3\ SiO_2 = 3\ CaSiO_3 + P_2O_5$$
$$P_2O_5 + 5\ C = 5\ CO + 2\ P.$$

Thus the calcium phosphate reacts with the finely divided silica to give calcium silicate and phosphoric oxide. The carbon and the phosphoric oxide then react to give phosphorus and carbon monoxide.

The phosphorus vapours and the carbon monoxide escape by means of the pipe E, and are condensed in water contained in copper vessels. Any oxidation of the phosphorus is prevented by passing a current of coal gas through the retorts and by the presence of the carbon monoxide produced during the reaction. The process is continuous, the fresh charge being added through a hopper B and carried by a screw arrangement D to the furnace. Fluxes are sometimes added to keep the calcium silicate molten; this collects at G and is withdrawn through F. Other types of furnaces are used, but the process is essentially the same.

351. Properties of Phosphorus.—The phosphorus so obtained is a pale yellow, translucent, crystalline solid which can be readily cut with a knife. On exposure to light it gradually darkens and finally becomes dark brown. It has a specific gravity of 1·82, it melts at 44° C., and boils at 287° C. It is insoluble in water, but readily dissolves in carbon disulphide, from which cubic crystals of white phosphorus are obtained on slow evaporation.

When white or yellow phosphorus is exposed to the air it slowly oxidises and emits white fumes (visible in the dark) consisting of a number of oxidation products, among which the following occur: phosphorus oxide (P_4O_6), phosphorus acid (H_3PO_3), phosphorus pentoxide (P_4O_{10}), phosphoric acid (H_3PO_4), and hypophosphoric acid ($H_4P_2O_6$): and for this reason it is kept under water. At the same time the phosphorus becomes faintly luminous and glows in the dark. The cause of this luminosity has not been established with

certainty, but it is probably connected in some way with the presence of ozone; this substance (along with hydrogen peroxide) is always produced during the slow oxidation of phosphorus, and it has been found that in the presence of bodies such as ether and turpentine which destroy ozone, the luminosity ceases. At 34° C. phosphorus ignites in air and burns with great brilliancy, forming phosphorus pentoxide, P_4O_{10}.

It should be mentioned that *perfectly dry air* (or oxygen) has no action on phosphorus at ordinary pressures, but if the pressure is reduced, or the oxygen is mixed with certain other gases, glowing occurs.

Phosphorus combines also at ordinary temperatures with fluorine, chlorine, bromine, iodine, and sulphur, and in the finely-divided condition with oxygen, with the evolution of light and heat.

Phosphorus reacts with metals to form *phosphides*. Thus *copper phosphide*, Cu_3P, is used in making phosphor-bronze. *Calcium phosphide*, Ca_3P_2, which is made by heating calcium phosphate with carbon in an electric furnace, is used for Holmes' Signals: they are made of a mixture of calcium carbide and calcium phosphide contained in a tin. When the tin is pierced and thrown into the sea, acetylene is produced and is ignited by the phosphine produced at the same time.

White phosphorus is very poisonous and the vapour causes a disease in which the bones of the jaw, etc., decay. For this reason white phosphorus is not used in the manufacture of matches.

Phosphorus may be obtained in three alloptropic modifications, white or yellow, red, and scarlet phosphorus.

352. Red Phosphorus.—Red Phosphorus is, according to its method of preparation, a reddish-brown powder or a close-textured mass showing a conchoidal fracture. This form is prepared on the large scale by heating ordinary phosphorus at 230° C.–250° C. for several hours in cast-iron pots, to which air has only limited access, and removing the unconverted phosphorus which remains by boiling the finely-divided product with caustic soda solution. On a small scale in the

laboratory it may readily be obtained by heating ordinary phosphorus in an atmosphere of nitrogen or carbon dioxide.

The red form of phosphorus differs very considerably in its properties from that already described. It has a higher specific gravity (2·1 to 2·34), and is insoluble in carbon disulphide. It undergoes no change in air at ordinary temperatures, and may be freely handled without danger; it combines with oxygen, the halogens and sulphur at much higher temperatures than ordinary phosphorus. Unlike ordinary phosphorus, it is not poisonous. Red phosphorus was formerly called "amorphous" phosphorus, but it has a crystalline structure.

353. The Transition Point: Red to Yellow Phosphorus; and Yellow to Red Phosphorus. (1) *Red to Yellow.*—When red phosphorus is heated to a temperature of 290° C. it vapourises to form the yellow variety. Also when red phosphorus is heated under increased pressure at 610° C. in an inert atmosphere it melts to give a yellow liquid. Red phosphorus is the more stable form, and at no temperature are the two forms in equilibrium. At ordinary temperatures yellow phosphorus is slowly changing into the red form, but the velocity of the change is so small that yellow phosphorus appears to be a stable allotrope.

(2) *Yellow to Red.*—When yellow phosphorus is heated to a temperature of 230° C.–250° C., but not above 250° C., in an inert atmosphere, red phosphorus is formed. The change is quicker if a *trace* of iodine, which acts as a catalyst, is present. It is an exothermic change and 3,700 calories are evolved.

354. Scarlet Phosphorus.—This is a form of phosphorus which is obtained by boiling a solution of ordinary phosphorus in phosphorus tribromide, when the phosphorus separates out as a scarlet precipitate called *Schenk's Scarlet phosphorus.* Scarlet phosphorus appears to be an amorphous form of the element. It possesses very active properties, being able, for example, to reduce copper sulphate to metallic copper. Scarlet phosphorus is *not poisonous.*

355. Violet or Metallic Phosphorus.—By heating red phosphorus with lead at about 500° C. for several hours, and then removing the lead by means of nitric acid, violet or metallic phosphorus is obtained. This form has a specific gravity equal to 2·34.

356. Matches.—Matches were first used by Chancel in Paris in 1805. They consisted of splints of wood with a tip at one end consisting of a mixture of sugar and potassium chlorate. They were ignited by dipping in sulphuric acid or by touching the tip with an asbestos pad soaked in sulphuric acid. Although Chancel's matches were cumbersome and inconvenient, they were used extensively until the introduction of the " friction " match.

In 1832, Sauria, Kammerer, and Preshel had independently discovered that a match with a head consisting of a mixture of potassium chlorate and antimony sulphide held together with gum, could be ignited by rubbing the head on paper covered with powdered glass, *i.e.* sand paper. They were named at first after an English artillery general, named Congreve. About the same time a mixture of yellow phosphorus, sulphur, and potassium chlorate was introduced for the head of the match, and although such matches were used for many years, they were found to be dangerous and poisonous. Later, legislation was introduced to prevent the use of white phosphorous, and the " safety " match became general.

The safety match, which was due to Professor Böttger and others, is made from a mixture of potassium chlorate, antimony sulphide, potassium dichromate, and gum, and is ignited by rubbing on a prepared surface consisting of *red* phosphorus, powdered sand or glass, antimony sulphide, and gum. Matches that " strike " on any roughened surface, are tipped with a mixture of scarlet phosphorus or a sulphide of phosphorus (P_4S_3 and P_3S_6), potassium chlorate, red lead, and gum.

357. Composition of the Phosphorus Molecule.—The vapour density of phosphorus (except at very high temperatures) is 62, and consequently its molecular weight is $2 \times 62 = 124$.

This is four times the atomic weight of phosphorus, and so a molecule of gaseous phosphorus contains four atoms, *i.e.* it is represented by P_4. At very high temperatures these molecules undergo partial dissociation into P_2 molecules.

Hydrides of Phosphorus.

358. The Three Compounds.—Phosphorus forms three hydrides—

Gaseous phosphoretted hydrogen or phosphine	PH_3.
Liquid phosphoretted hydrogen	P_2H_4.
Solid phosphoretted hydrogen	$P_{12}H_6$.

359. Phosphorus Trihydride, or Phosphine, PH_3.—This gas was discovered accidentally by Gengembre in 1783 in an attempt to prepare "liver of phosphorus," by the action of phosphorus on caustic potash. It is the analogue of ammonia, and is obtained by Gengembre's method. Prepared in this way, it is mixed with small quantities of the liquid and solid hydrides, the former of which renders it spontaneously inflammable in air. To prevent the gas taking fire in the flask, the air is displaced from the apparatus by coal gas before heating. The end of the delivery tube dips under water as shown in Fig. 71, and as each bubble of gas reaches the surface it inflames and produces a ring of white smoke (phosphorus pentoxide).

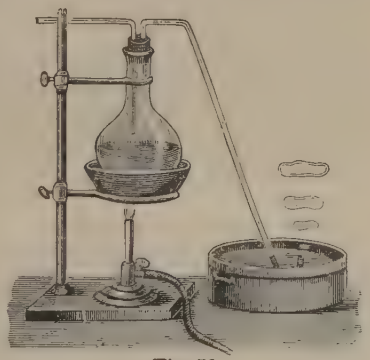


Fig. 71.

The reaction which takes place is—

$$4\,P + 3\,NaOH + 3\,H_2O = 3\,\underset{\text{Sodium hypophosphite.}}{NaH_2PO_2} + PH_3.$$

Phosphine may also be prepared by heating phosphorous acid, H_3PO_3—

$$4\ H_3PO_3 = PH_3 + 3\ H_3PO_4,$$

or by the action of water on calcium phosphide, Ca_3P_2—

$$Ca_3P_2 + 6\ H_2O = 3\ Ca(OH)_2 + 2\ PH_3.$$

Pure phosphorus trihydride may be prepared by treating phosphonium iodide, PH_4I (see below), with caustic potash or soda, the reaction being analogous to that employed in the preparation of ammonia—

$$PH_4I + NaOH = PH_3 + NaI + H_2O$$

$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O.$$

The gas may be collected over water.

360. Properties of PH_3.—It is a colourless gas which condenses when cooled to — 86° C. It is very slightly soluble in water, and possesses a penetrating garlic-like odour which is evident even with very small quantities of the gas ; it is very poisonous. If free from other hydrides, it is not inflammable in air at ordinary temperatures ; heat decomposes the gas into its elements more readily than the corresponding nitrogen compound, NH_3.

361. Phosphonium Compounds.—Just as ammonia combines directly with the haloid acids, HCl, HBr, etc., to form ammonium chloride, ammonium bromide, etc., so phosphorus trihydride forms similar compounds called *phosphonium* compounds. The corresponding hydroxide, $PH_4(OH)$, however, is not known. The combination with hydriodic acid to form phosphonium iodide—

$$PH_3 + HI = PH_4I,$$

takes place very readily.

Phosphonium iodide is the most important phosphonium compound, and may be prepared readily by the following method :—Phosphorus and iodine are mixed with carbon disulphide in a retort. The carbon disulphide is then removed by distillation. The product is decomposed by water, the air

of the apparatus being displaced by an atmosphere of carbon dioxide. The phosphonium iodide is finally sublimed and condensed in a wide tube—

$$5\,I + 9\,P + 16\,H_2O = 5\,PH_4I + 4\,H_3PO_4.$$

Phosphonium iodide consists of colourless crystals. On heating it dissociates into phosphine and hydrogen iodide ($CfNH_4I$)—

$$PH_4I \rightleftharpoons PH_3 + HI.$$

It is decomposed by water giving phosphine (see § 359). Phosphonium iodide is used as a reducing agent, and in organic chemistry. Phosphonium bromide and phosphonium chloride are similar compounds, but much less stable at ordinary temperatures.

362. Liquid Phosphoretted Hydrogen.—P_2H_4 is prepared by passing the gases produced by the action of warm water on calcium phosphide, first through a spiral tube to condense the water and then through a vessel surrounded by a freezing mixture. The liquid is spontaneously inflammable in air, has a density of 1·01, and boils at 57-58° C. (735 mm.).

363. Solid Phosphoretted Hydrogen, $P_{12}H_6$, is obtained when liquid phosphoretted hydrogen is exposed to light, or heated above its boiling point—

$$15\,P_2H_4 = P_{12}H_6 + 18\,PH_3.$$

Obtained in this way, it is a yellow powder insoluble in water, and with feeble acidic properties. On heating in a stream of carbon dioxide it is readily decomposed into hydrogen and phosphorus. If heated in vacuo a red substance is said to be formed, viz. P_9H_2.

Phosphorus and Oxygen.

364. The Various Compounds.—A list of the oxides and oxyacids of phosphorus which are known is given in the following table:—

Oxides.	Corresponding Acids.
P_4O Phosphorus suboxide	———
$[P_2O]$ not known in the free state ...	Hypophosphorous acid, H_3PO_2 or $P_2O{\cdot}3\ H_2O$
P_2O_3 Phosphorous oxide	Phosphorous acid, H_3PO_3 or $P_2O_3.3\ H_2O$
P_2O_4 Phosphorus dioxide or Phosphorus tetroxide) ...	Hypophosphoric acid, $H_4P_2O_6$ or $P_2O_4.2\ H_2O$
P_2O_5 Phosphoric oxide (or phosphorus pentoxide) ...	*Ortho*-phosphoric acid, H_3PO_4 or $P_2O_5.3\ H_2O$ *Meta*-phosphoric acid, HPO_3 or $P_2O_5.H_2O$ *Pyro*-phosphoric acid, $H_4P_2O_7$ or $P_2O_5.2\ H_2O$ Per*mono*phosphoric acid, H_3PO_5 Per*di*phosphoric acid, $H_4P_2O_8$

The more important are phosphorous oxide, P_2O_3, phosphorus pentoxide, P_2O_5, and the acids derived from them.

365. Phosphorus Suboxide, P_4O.—There is some doubt as to the existence of this compound. It is said to be obtained as a red to yellow substance (1) when phosphorus is heated in a slow current of air, or (2) by the decomposition of phosphorous oxide.

366. Phosphorous Oxide, P_4O_6 : Preparation.—Phosphorous oxide is obtained mixed with phosphorus pentoxide when phosphorus is exposed to oxidation in air at ordinary temperature, or when it is burnt in a limited supply of air. Its preparation is carried out in the following manner :—

A glass tube is drawn out into the shape shown at A, Fig. 72, and some pieces of phosphorus are introduced into it. This tube is connected with a metal condenser D, the inner tube of which is provided with a plug of glass wool at the end away from A ; the space between the two tubes of the condenser is filled with water. The condenser is attached to a U-tube C connected at its lower end with a bottle E, as shown in the

diagram ; the U-tube and bottle are surrounded by a freezing mixture of ice and salt. The tube A is gently heated and a current of air is drawn through the apparatus by means of an aspirator attached to the U-tube.

The phosphorus melts, but is prevented from running out by the shape of the tube ; it burns in the current of air and a mixture of P_4O_6 and P_2O_5 passes over into D, where it condenses. After some time the condenser is heated till the temperature of the water rises to 50° C. as indicated by the thermometer, T. This temperature is sufficient to melt the phosphorous oxide which passes over into the U-tube, where it solidifies, but the phosphorus pentoxide remains solid and the plug of glass wool keeps it back in D. Occasionally the freezing mixture is removed from the U-tube and bottle, and the U-tube is gently warmed, when the P_4O_6 melts and runs down into bottle.

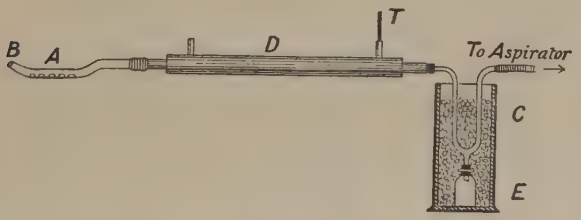


Fig. 72.

367. Properties of Phosphorous Oxide.—Phosphorous oxide is a white crystalline solid, melting at 21° C. to a colourless liquid of density 1·936. It has a garlic-like odour and is highly poisonous. Phosphorous oxide is slowly dissolved by *cold* water with formation of phosphorous acid, H_3PO_3, and is therefore the anhydride of this acid—

$$P_4O_6 + 6\,H_2O = 4\,H_3PO_3.$$

With *hot* water, however, a violent reaction takes place with formation of red phosphorus, phosphides of hydrogen, and phosphoric acid—

$$P_4O_6 + 6\,H_2O = PH_3 + 3\,H_3PO_4.$$

On exposure to moist air or oxygen it oxidises to phosphorus pentoxide, and if the temperature is slightly raised it takes fire.

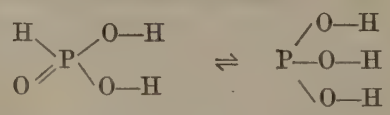
The vapour density of phosphorous oxide is 110, and consequently its molecular weight is $2 \times 110 = 220$. This corresponds to a formula P_4O_6 for the gaseous molecule ($P_4 = 4 \times 31 = 124$, $O_6 = 6 \times 16 = 96$, and $124 + 96 = 220$).

368. Phosphorous Acid, H_3PO_3: Preparation.—This acid may be obtained, as already stated, by the action of cold water on phosphorous oxide. It is prepared by the action of water on phosphorus trichloride—

$$PCl_3 + 3\,H_2O = H_3PO_3 + 3\,HCl.$$

It is not necessary to actually prepare the trichloride, and the most convenient course of procedure is to pass chlorine into phosphorus melted under a layer of water. A solution of phosphorous acid is thus obtained, and on concentrating and allowing to cool, crystals of the acid separate out.

369. Properties of Phosphorous Acid.—Phosphorous acid is a white, deliquescent crystalline solid, melting at 70° C. It is a *tribasic* acid, but only two of the three hydrogen atoms in the molecule of phosphorous acid are usually replaceable by metals, to form *phosphites*. Thus it forms salts such as KH_2PO_3, K_2HPO_3, and Ag_2HPO_3, but Ag_3PO_3 and K_3PO_3 have not been prepared. Organic derivatives, *e.g.* $P(OC_2H_5)_3$ triethyl phosphite have been obtained, and Na_3PO_3 has been prepared. These facts can be explained by assuming an equilibrium mixture of the two forms—



On heating, phosphorous acid decomposes, yielding phosphoric acid and phosphine—

$$4\,H_3PO_3 = 3\,H_3PO_4 + PH_3.$$

It is a strong reducing agent, as it readily takes up oxygen and is transformed into ordinary phosphoric acid, H_3PO_4.

Thus it precipitates metallic copper from a solution of copper sulphate on boiling, and precipitates gold and silver from solutions of their salts.

370. Phosphorus Pentoxide, P_4O_{10}: Preparation.—Whenever phosphorus is burnt in an excess of dry oxygen or air this oxide is formed. The operation may be performed in a glass bolt-head with two side tubes, through one of which passes air dried over fused calcium chloride, and through the other the fumes are aspirated, a bottle being placed between the aspirator and the side tube to intercept the phosphorus pentoxide (Fig. 73).

A small piece of phosphorus carefully dried between filter paper is introduced through the neck of the bolt-head into a small basin attached as shown, and then successively other pieces, until sufficient of the oxide has been prepared. After the first piece has been ignited by touching it with a hot wire, the basin will be hot enough to start the combustion of the subsequent portions as they are dropped into it. The pentoxide so obtained always contains phosphorous oxide, from which it may be freed by passing it in the gaseous form along with oxygen over gently heated finely-divided platinum. Compare the preparation of sulphur trioxide—

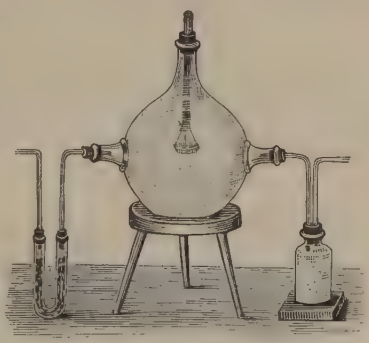


Fig. 73.

$$P_4 + 5\ O_2 = P_4O_{10} + 740{,}000 \text{ calories.}$$

As will be seen from the equation, the reaction is strongly exothermic.

371. Properties of Phosphorus Pentoxide.—The oxide is an amorphous white powder, which when left in contact with moist air gradually absorbs moisture and deliquesces. It

combines with water in the cold with the liberation of much heat and with a hissing noise, to form metaphosphoric acid, HPO_3—

$$P_4O_{10} + 2\,H_2O = 4\,HPO_3 + 70{,}000 \text{ calories.}$$

It is also the anhydride of orthophosphoric and pyrophosphoric acids. Thus if the water is hot, orthophosphoric acid is formed—

$$P_4O_{10} + 6\,H_2O = 4\,H_3PO_4.$$

Its great affinity for water renders it a valuable agent for completely drying gases, whilst in contact with acids it frequently deprives them of water, forming anhydrides—

$$2\,H_2SO_4 + P_4O_{10} = 4\,HPO_3 + 2\,SO_3$$
$$4\,HNO_3 + P_4O_{10} = 4\,HPO_3 + 2\,N_2O_5.$$

Similarly it chars wood, paper, and many organic substances by its dehydrating action. It has been used to prepare carbon suboxide, C_3O_2, from malonic acid—

$$CH_2(COOH)_2 + P_2O_5 = C_3O_2 + H_4P_2O_7.$$

372. Orthophosphoric Acid (Ordinary Phosphoric Acid), H_3PO_4 : Preparation.—Orthophosphoric acid is obtained by dissolving phosphorus pentoxide in water and boiling the solution. It is generally prepared by the action of nitric acid on ordinary phosphorus, or by boiling for some time a solution of metaphosphoric acid—

$$HPO_3 + H_2O = H_3PO_4.$$

It may also be prepared by treating calcium phosphate with the calculated amount of sulphuric acid, filtering off the precipitated calcium sulphate and concentrating the solution—

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 = 3\,CaSO_4 + 2\,H_3PO_4.$$

Exp. 98.—Introduce about 10 grm. of red phosphorus into a large retort, and cover it with concentrated nitric acid. Place a flask over the mouth of the retort. Now heat cautiously, and presently red fumes of oxides of nitrogen will be evolved by the reduction of the nitric acid—

$$4\,P + 10\,HNO_3 + H_2O = 4\,H_3PO_4 + 5\,NO + 5\,NO_2.$$

Continue the heating in such a manner as to keep the liquid about its boiling-point, but so that as little as possible distils over. When the

phosphorus has all disappeared, and red fumes are no longer generated, distil the acid over until that remaining has a syrupy consistency; more red fumes will be evolved at this stage through the oxidation of some phosphorous acid. Finally, transfer the thick liquid to a porcelain dish and evaporate so long as strongly acid fumes (HNO_3) are given off.

As trichloride of phosphorus when treated with excess of water yields phosphorous acid, so the pentachloride, by similar treatment, gives ordinary phosphoric acid—

$$PCl_5 + 4\,H_2O = H_3PO_4 + 5\,HCl.$$

The aqueous solution, if concentrated until the temperature rises to 140° C., and then allowed to cool in a desiccator, crystallises on standing.

373. Properties of Phosphoric Acid.—Phosphoric acid is a colourless deliquescent crystalline solid, melting at 41·7° C.; the crystals consist of hard rhombic prisms. Phosphoric acid is soluble in water to give a feebly acid solution, and ionises mainly thus—

$$H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4'.$$

The further ionisation of the H_2PO_4 ion is very small. It is, however, a tribasic acid, each of the atoms of hydrogen being replaceable by a metal.

374. The Phosphates.—The phosphates of the alkali metals sodium, potassium, and of ammonium are soluble in water, and are obtained by the addition of the alkali hydroxides to phosphoric acid. The amount of the alkali added may be sufficient to replace one, two, or three atoms of the hydrogen, thus—

$$\underset{40}{NaOH} + \underset{98}{H_3PO_4} = \underset{\text{Sodium dihydrogen phosphate.}}{NaH_2PO_4} + H_2O$$

$$\underset{80}{2\,NaOH} + \underset{98}{H_3PO_4} = \underset{\text{Disodium hydrogen phosphate.}}{Na_2HPO_4} + 2\,H_2O$$

$$\underset{120}{3\,NaOH} + \underset{98}{H_3PO_4} = \underset{\text{Normal sodium phosphate.}}{Na_3PO_4} + 3\,H_2O.$$

The numbers underneath show the combining proportions of caustic soda and phosphoric acid required to form such

salts. That is to say, if to 98 grm. of phosphoric acid there be added 40 grm. of caustic soda and the solution evaporated the salt NaH_2PO_4 will be obtained; if 80 grm., then the salt formed will be Na_2HPO_4, and if 120 grm., the salt Na_3PO_4 will be formed.

Na_3PO_4 is an example of a *normal* salt which is *not neutral* in its reaction with litmus but *alkaline*.

NaH_2PO_4, Sodium dihydrogen phosphate—slightly acid reaction.

Na_2HPO_4, Disodium hydrogen phosphate—slightly alkaline.

Na_3PO_4, Normal sodium phosphate—distinctly alkaline.

An explanation of these phenomena can be given on the basis of the ionic theory. Thus normal sodium phosphate, Na_3PO_4, ionises to a great extent in solution thus—

$$Na_3PO_4 \rightleftharpoons 3\,Na^{\cdot} + PO_4'''.$$

Now the PO_4''' ions present combine with the hydrogen ions present to form H_2PO_4 ions. In this way the solution is therefore rich in OH ions. The equilibrium—

$$H_2O \rightleftharpoons H^{\cdot} + OH^{\cdot}$$

is thus upset, and hence more molecules of water ionise to hydrogen and hydroxyl ions. Then more hydrogen ions are available for PO_4''' ions, and this process goes on until nearly all the PO_4 ions are converted to H_2PO_4 ions.

Hence the solution is richer in OH ions than in H ions, and therefore gives an alkaline reaction.

The salt ordinarily known as "sodium phosphate" is Na_2HPO_4.

In "microcosmic salt" part of the hydrogen is replaced by sodium and part by ammonium, $Na{\cdot}NH_4{\cdot}HPO_4$.

The normal phosphates of the alkaline earth metals (Ba, Sr, Ca) and of Mg, Pb, Ag, and indeed of all other metals, are insoluble in water, but soluble in dilute mineral acids. They may be prepared by adding a soluble salt of the metal in question to an aqueous solution of an alkali phosphate—

$$2\,Na_3PO_4 + 3\,CaCl_2 = Ca_3(PO_4)_2 + 6\,NaCl.$$

$$Na_3PO_4 + 3\,AgNO_3 = Ag_3PO_4 + 3\,NaNO_3.$$

375. Tests for Phosphates.—(1) Ferric chloride gives, even in presence of acetic acid, a yellowish-white precipitate of ferric phosphate. (Arsenates also give a yellowish-white precipitate.)

(2) Silver nitrate gives a pale yellow precipitate of silver phosphate. (Arsenates give a brick-red precipitate.)

(3) Excess of ammonium molybdate in the presence of nitric acid gives a bright yellow precipitate of phosphomolybdate of ammonium even in the cold, but more rapidly on warming. (The arsenates give a similar precipitate only on warming.)

(4) The presence of phosphorus may always be detected by heating a little of the powdered substance along with magnesium filings in a narrow tube and then moistening the product with water. Phosphoretted hydrogen is given off, and may be recognised by its characteristic odour.

376. Pyrophosphoric Acid, $H_4P_2O_7$.—This is obtained as a glassy mass by cautiously heating ordinary phosphoric acid to 215° C.—

$$2\,H_3PO_4 = H_4P_2O_7 + H_2O.$$

It is a white crystalline solid melting at 61° C. and is readily soluble in water. The aqueous solution is slowly converted into orthophosphoric acid at the ordinary temperature, but more rapidly on boiling—

$$H_4P_2O_7 + H_2O = 2\,H_3PO_4.$$

It is a tetrabasic acid. The pyrophosphates are most readily made by heating the corresponding monohydrogen phosphate, *e.g.*—

$$2\,Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Magnesium pyrophosphate, $Mg_2P_2O_7$ is an important salt and is used in the estimation both of magnesium and of phosphoric acid.

As with the phosphates, the salts of the alkali metals are soluble in water, those of the other metals being insoluble in water but soluble in dilute mineral acids.

Tests for Pyrophosphates.—(1) Silver nitrate gives a *white* precipitate of $Ag_4P_2O_7$ (distinction from phosphates).

(2) Pyrophosphoric acid does not coagulate albumen (distinction from metaphosphoric acid).

(3) Cadmium chloride in the presence of acetic acid gives a white precipitate (distinction from the other phosphoric acids).

377. Metaphosphoric Acid, HPO_3.—This is obtained when ortho- or pyrophosphoric acid or their ammonium salts are strongly heated—

$$H_3PO_4 = HPO_3 + H_2O.$$

It is a glassy solid (whence the name *glacial phosphoric acid* by which it is also known) and closely resembles pyrophosphoric acid in appearance. It is readily soluble in water, and in solution passes slowly into orthophosphoric acid; on heating the change takes place rapidly—

$$HPO_3 + H_2O = H_3PO_4.$$

The salts of HPO_3 resemble those of H_3PO_4 and $H_4P_2O_7$ as regards their solubility in water and acids.

Sodium metaphosphate, $NaPO_3$ is readily prepared by heating microcosmic salt—

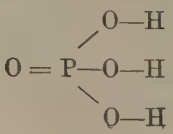
$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O.$$

It is important as it is used sometimes for the bead test in analysis in the place of borax.

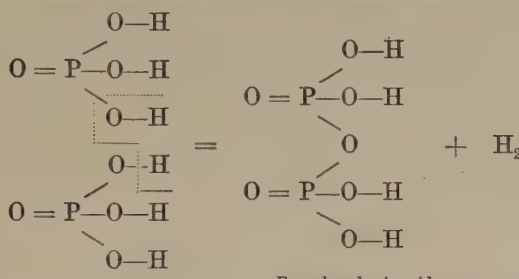
Tests for Metaphosphates.—(1) Silver nitrate gives a *white* precipitate of $AgPO_3$ (distinction for phosphates).

(2) Metaphosphoric acid coagulates albumen (distinction from ortho- and pyrophosphoric acids).

378. Constitution of the Phosphoric Acids.—Orthophosphoric acid is represented by the constitutional formula—



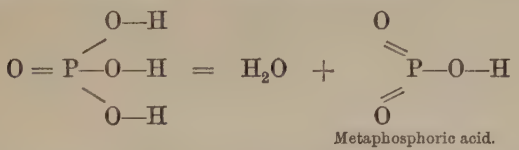
To arrive at the constitution of pyrophosphoric acid we must remember that it is formed by the loss of one molecule of water from two molecules of the ortho-acid—



Pyrophosphoric acid.

This represents pyrophosphoric acid as a tetrabasic acid, for it has *four* hydroxyl groups; the basicity as determined by experiment is found to agree with this.

Metaphosphoric acid is produced by a further loss of water, and its formation may be thus represented—



Metaphosphoric acid.

379. Hypophosphorous Acid, H_3PO_2.—This is obtained by the action of the calculated quantity of sulphuric acid on its barium salt obtained as below—

$$\underset{\text{Barium hypophosphite.}}{Ba(H_2PO_2)_2} + H_2SO_4 = BaSO_4 + 2\,H_3PO_2.$$

The solution is filtered to remove the barium sulphate, and on evaporation under reduced pressure, crystals of hypophosphorous acid are obtained, melting at 26·5° C.

The barium salt is prepared by boiling phosphorus with a solution of barium hydroxide—

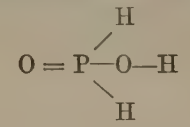
$$6\,H_2O + 3\,Ba(OH)_2 + 2\,P_4 = 3\,Ba(H_2PO_2)_2 + 2\,PH_3.$$

Hypophosphorous acid is a white, crystalline solid, soluble in water to give a weak acid. It readily takes up oxygen with formation of acids containing more oxygen, and on this account possesses strong reducing properties. Thus, on exposure to the air oxygen is gradually absorbed and phosphorous and phosphoric acids are produced ; again, on heating with copper sulphate, copper hydride, Cu_2H_2, is formed as a red precipitate. It is a monobasic acid and forms hypophosphites.

On heating, hypophosphorous acid and its salts are converted into phosphoric acid or phosphates with liberation of phosphine—

$$2\,H_3PO_2 = H_3PO_4 + PH_3.$$

Hypophosphites are used extensively in medicine. A mixture of the hypophosphites of calcium, potassium, and sodium is used in "Parrish's Chemical Food." The constitutional formula of hypophosphorous acid is probably—



380. Phosphorus Tetroxide, P_2O_4.—This is obtained by heating phosphorous oxide in a sealed tube to 440° C.—

$$4\,P_4O_6 = 6\,P_2O_4 + P_4.$$

The tetroxide forms a sublimate of colourless crystals, which are very deliquescent, and dissolve in water with formation of phosphoric and phosphorous acids—

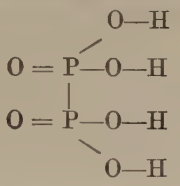
$$P_2O_4 + 3\,H_2O = H_3PO_3 + H_3PO_4.$$

381. Hypophosphoric Acid, $H_4P_2O_6$.—This is *not* formed by the action of water on P_2O_4, so that it cannot strictly be called the acid corresponding to this oxide as in the table on p. 368. It is one of the products of the slow oxidation of phosphorus, and can be prepared by decomposing lead hypophosphate, $Pb_2P_2O_6$, with hydrogen sulphide—

$$Pb_2P_2O_6 + 2\,H_2S = H_4P_2O_6 + 2\,PbS.$$

Hypophosphoric acid is a crystalline solid decomposing on heating into metaphosphoric and phosphorous acids and phosphine.

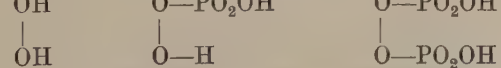
It is a tetrabasic acid and probably has the constitutional formula—



382. Reactions of the Phosphoric Acids.—The reactions are shown in the following table :—

Reagent.	Hypo Phosphites (H_3PO_2)	Ortho-phosphates (H_3PO_4)	Pyro-phosphates ($H_4P_2P_7$)	Meta-phosphates (HPO_3)
Silver nitrate (neutral)	Ppt. of Ag	Yellow ppt. Ag_3PO_4	White crystalline ppt. $Ag_4P_2O_7$	White gelatinous ppt. $AgPO_3$
Barium-chloride ...	White ppt. BaH_2PO_2	White ppt. $Ba_3(PO_4)_2$ Sol. in acetic acid	White ppt. $Ba_2P_2O_7$ Insol. in acetic acid	White ppt. $Ba(PO_3)_2$ Insol. in acetic acid Sol. in excess of $NaPO_3$
Albumen	←	Nil	→	Coagulation
Copper sulphate (acid)	Brown ppt. Cu_2H_2	—	—	—
Magnesium chloride ... (NH_4OH and NH_4Cl present) ...	White ppt.	White ppt.	White ppt. Sol. in excess	No ppt.

383. The Per-Phosphoric Acids.—The per-phosphoric acids can be considered to be derivatives of hydrogen peroxide—



Per*mono*phosphonic acid. Per*di*phosphoric acid.

As shown above they are called per*mono*phosphoric acid, H_3PO_5 and per-*di*-phosphoric acid, $H_4P_2O_8$, and are analogous to the per-sulphuric acids (§ 336). Their potassium salts are prepared by the electrolysis of solutions of di-potassium phosphate to which are added a little potassium fluoride and potassium dichromate; the products formed depend on the current density, thus with a lower current density the per-di-salt is the main product, whereas with a higher current density the per-mono-salt predominates. The acids and the salts behave similarly to the corresponding sulphur compounds.

Compounds of Phosphorus with the Halogens.

384. The Various Compounds.—By direct union of phosphorus with these elements, bodies of the type PX_3 and PX_5 are formed, and by the action of moisture on PCl_5 and PBr_5, the oxychloride $POCl_3$, and oxybromide $POBr_3$, respectively, are obtained.

It will be seen that in these compounds phosphorus is either tervalent or quinquevalent.

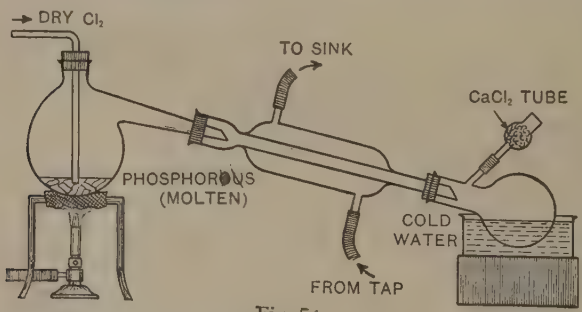


Fig. 74.

385. Phosphorus Trichloride, PCl_3.—This compound is prepared by passing dry chlorine over red or yellow phosphorus heated in a glass retort; the trichloride distils over and is collected in a receiver cooled by water, and in this

way is freed from the pentachloride. A suitable apparatus is shown in Fig. 74.

Properties.—Phosphorus trichloride is a colourless mobile liquid boiling at 76° C., and freezing at − 112° C. It fumes in moist air, and has an acrid, pungent odour. Phosphorus trichloride is decomposed by water with formation of phosphorous and hydrochloric acids—

$$PCl_3 + 3\,H_2O = H_3PO_3 + 3\,HCl.$$

It combines directly with chlorine to form phosphorus pentachloride— $PCl_3 + Cl_2 = PCl_5$.

It is used extensively in organic chemistry for the replacement of hydroxyl groups by chlorine. Thus with ethyl alcohol ethyl chloride is formed—

$$3\,C_2H_5OH + PCl_3 = 3\,C_2H_5Cl + P(OH)_3.$$

With sulphur trioxide, phosphorus oxychloride and sulphur dioxide are formed—

$$SO_3 + PCl_3 = POCl_3 + SO_2.$$

Phosphorus tribromide, PBr_3, and *phosphorus triiodide*, PI_3, have similar properties.

386. Phosphorus Pentachloride, PCl_5.—Phosphorus pentachloride is prepared by—

(1) The reaction of phosphorus trichloride and excess of dry chlorine. A convenient apparatus is shown in Fig. 75. It may also be prepared by—

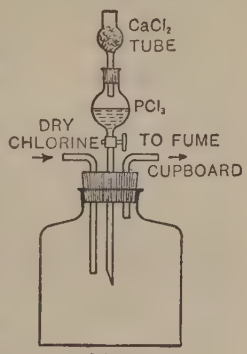


Fig. 75.

(2) Passing dry chlorine through a well cooled solution of phosphorus in carbon disulphide.

(3) The action of sulphur chloride on phosphorus trichloride in the presence of a trace of iodine—

$$S_2Cl_2 + 3\,PCl_3 = PCl_5 + 2\,PSCl_3.$$

Properties.—The pentachloride is a light yellow solid, which fumes in moist air and sublimes on heating, undergoing

partial dissociation into PCl_3 and Cl_2. With a small quantity of water phosphorus pentachloride yields phosphorus oxychloride—

$$PCl_5 + H_2O = POCl_3 + 2\,HCl;$$

but with excess of water phosphoric acid is formed—

$$POCl_3 + 3\,H_2O = PO(OH)_3 + 3\,HCl;$$

or, writing both stages in one equation—

$$PCl_5 + 4\,H_2O = PO(OH)_3 + 5\,HCl.$$

The greater attraction which phosphorus has for oxygen than for chlorine renders PCl_5 a valuable reagent for substituting chlorine for oxygen or hydroxyl, with elimination of HCl. It is much used for this purpose in dealing with carbon compounds. Examples of such actions are given in the following equations :—

$$SO_2 + PCl_5 = POCl_3 + SOCl_2.$$

$$SO_2(OH)_2 + PCl_5 = POCl_3 + SO_2(OH)Cl + HCl.$$

$$SO_2(OH)Cl + PCl_5 = POCl_3 + SO_2Cl_2 + HCl.$$

$$\underset{\text{Ethyl alcohol.}}{C_2H_5\cdot OH} + PCl_5 = POCl_3 + \underset{\text{Ethyl chloride.}}{C_2H_5\cdot Cl} + HCl.$$

$$\underset{\text{Acetic acid.}}{C_2H_3O\cdot OH} + PCl_5 = POCl_3 + \underset{\text{Acetyl chloride}}{C_2H_3O\cdot Cl} + HCl.$$

$$\underset{\text{Aldehyde.}}{CH_3CHO} + PCl_5 = POCl_3 + \underset{\text{Ethylidene chloride.}}{CH_3CHCl_2}.$$

Phosphorus pentabromide, PBr_5, a yellow crystalline solid, and phosphorus pentafluoride, PF_5, a colourless gas, have similar properties. The pentaiodide is not known, and the pentafluoride is the most stable of this series of compounds.

387. Phosphorus Oxychloride, $POCl_3$.—As already stated, this compound is obtained when phosphorus pentachloride is treated with a small quantity of water, and a number of reactions have just been given in which it is produced.

A method which gives practically a quantitative yield,

consists in heating phosphorus trichloride with potassium chlorate—

$$3\ PCl_3 + KClO_3 = 3\ POCl_3 + KCl.$$

The $POCl_3$ can be separated by distilling gently.

It may also be prepared by heating a mixture of phosphorus pentoxide and phosphorus pentachloride under pressure—

$$3\ PCl_5 + P_2O_5 = 5\ POCl_3.$$

It is a colourless liquid boiling at 107° C., and is decomposed by water according to the equation—

$$POCl_3 + 3\ H_2O = PO(OH)_3 + 3\ HCl.$$

QUESTIONS.—CHAPTER XXI.

1. State what you know of the history of the element phosphorus ?

2. What is the effect of heating chlorapatite and fluorapatite respectively with concentrated sulphuric acid ?

3. How is phosphorus extracted from bone-ash ?

4. Describe the electric process for the manufacture of phosphorus from bone-ash.

5. Discuss the nature of the changes which take place when phosphorus undergoes slow oxidation in air.

6. Write down in parallel columns the physical properties of ordinary and red phosphorus.

7. What differences are there in chemical behaviour between ordinary and red phosphorus ?

8. Why does a match ignite when rubbed on a rough surface ? What chemical action takes place during the ignition ?

9. To what is the spontaneous ignition of phosphorus trihydride prepared from phosphorus and caustic soda due, and how may the hydride be prepared so as not to ignite spontaneously ?

10. Express by equations the action of phosphorus on chlorine, iodine, caustic potash, and nitric acid.

11. Compare the trihydride of phosphorus with the trihydride of nitrogen.

12. How is phosphorous oxide prepared, and how may it be converted into the pentoxide ?

13. What is the action of (*a*) cold water, (*b*) hot water on phosphorous oxide ?

14. How has it been proved that the formula for phosphorous oxide is P_4O_6, not P_2O_3?

15. Describe the preparation and properties of phosphorous acid.

16. How may phosphorus pentoxide be obtained in quantity and converted into metaphosphoric acid and into phosphoric acid?

17. What is the action of water on the trichloride and on the pentachloride of phosphorus? Give equations.

18. Describe in detail the preparation of phosphoric acid from phosphorus.

19. What is meant by saying that orthophosphoric acid is a *tribasic* acid? Write down the names and formulae of a few phosphates that are soluble in water.

20. By what chemical tests may phosphates be distinguished from arsenates and from pyrophosphates?

21. How are metaphosphoric and pyrophosphoric acids prepared and distinguished?

22. Write down the constitutional formulae of the acids of phosphorus of which P_2O_5 is the anhydride.

23. How is hypophosphorous acid prepared, and what are its chief properties? Write down the constitutional formulae for this acid.

24. Describe the preparation of the chlorides of phosphorus and of phosphorus oxychloride.

25. 50 grm. of caustic soda are mixed with 61·25 grm. of orthophosphoric acid. What salt will be produced and how much of it will be obtained?

(Na = 23, O = 16, H = 1, P = 31.)

CHAPTER XXII.

CARBON AND THE HYDROCARBONS.

388. General Characteristics of the Carbon Group.—Carbon is the first member of a group consisting of the elements carbon, silicon, titanium, zirconium, and thorium, of which the first two members alone come under consideration amongst the non-metals. They show a considerable resemblance to one another in their physical and chemical properties.

Comparing together more particularly carbon and silicon we observe that—

(1) The elements themselves are very infusible.

(2) They exist in allotropic modifications of similar character.

(3) They form oxides of great stability and also gaseous hydrides, CH_4 and SiH_4, the former of these being a stable body, whilst the latter undergoes decomposition very readily.

(4) Carbon and silicon both combine directly with fluorine to form CF_4 and SiF_4 respectively. With the other halogen elements they do not combine directly, but volatile liquid tetrachlorides, CCl_4 and $SiCl_4$, are obtained indirectly.

389. Carbon: History.—Carbon in the form of charcoal and probably diamond have been known for ages. The combustibility of the diamond was first demonstrated in 1694 by two Italians, Averani and Targioni. Lavoisier, in 1775, however, was the first to prove that diamond was a form of carbon. Later, Tennant, in 1797, showed that on the combustion of diamond carbon dioxide alone is produced and he conducted quantitative experiments to prove that equal

weights of diamond and charcoal on combustion, produced equal quantities of carbon dioxide. Davy, in 1814, confirmed this result.

Graphite or plumbago, previous to 1800, was confused with molybdenum sulphide, but in that year Mackenzie proved that it was a crystalline form of carbon.

390. Occurrence.—Carbon is found in nature in a state of comparative purity as diamond and graphite, the latter known as mineral plumbago, from which black-lead pencils are made. These forms do not, however, occur in any very considerable quantity, and the sources from which the large supplies of carbon are obtained are coal and vegetable matter.

In combination it is found very extensively as carbonates (limestone, dolomite, etc.); as carbon dioxide in the atmosphere; as hydrocarbons (§ 407) in petroleum and natural gas, and as organic compounds in all plant and animal tissue.

391. Allotropic Forms of Carbon.—Carbon exists in three allotropic modifications; diamond, graphite, and charcoal. These forms are described separately in the following pages.

392. Diamond.—Diamond is a *crystalline* form of carbon. It is found chiefly in South Africa, Brazil, and Australia. Diamonds in South Africa usually occur in the "blue earth" in "conical pipes," which are considered to have been formed by volcanic agencies. The conical pipes are mined and the "earth" brought to the surface to be weathered, until it is a coarse powder. The powder is then washed with water when the lighter materials are removed and the product is passed over a layer of grease which causes the diamonds to adhere and remain behind.

These natural diamonds are of varying size and colour, and include black diamonds or carbonado. The Cullinan diamond was the largest that has been discovered, and weighed 3,032 carats when found at Pretoria in 1905. The crude diamonds are cut so that "facets" are formed; the value of diamonds depends on the colour, the weight, and their effect on light.

393. Properties of Diamond.—Diamond consists of practically pure carbon, 12 parts by weight of diamond yielding on combustion 44 parts of carbon dioxide according to the equation—

$$C + O_2 = CO_2.$$

The diamond crystallises in the cubic system. The structure of the crystals has been shown by X-rays spectra to be such that a carbon atom is situated at each of the four corners of a regular tetrahedron and one carbon atom at the centre of the tetrahedron.

Diamond is the densest form of carbon with specific gravity about 3·5 and has a refractive index 2·45. It is the hardest known substance, and it is this property and its brilliancy of lustre when cut, that make it so valuable. It is the most difficult of the allotropes of carbon to ignite in oxygen (ca 800° C.). Towards the usual reagents it is very stable. It is unaffected by acids but is slowly attacked by fused sodium carbonate as shown by the equation—

$$C + Na_2CO_3 = Na_2O + 2\,CO.$$

394. The Formation of Diamonds.—Diamonds are believed to have crystallised from molten carbon, under great pressure. These conditions are said to have been present by geologists, after studying the media in which diamonds occur. The artificial preparation of diamonds by Moissan and the occurrence of diamonds in meteorites support this view.

Moissan, in 1893, succeeded in preparing small diamonds artificially from charcoal by means of the electric furnace. Iron and carbon are placed in a crucible which is then introduced into an electric furnace and raised to a high temperature. The iron melts and dissolves the carbon; on now placing the crucible in a bath of molten lead the outer layer of iron solidifies, contracts, and in so doing exerts great pressure on the still liquid metal inside. Under these conditions some of the carbon crystallises out in the form of diamond. The iron is dissolved in hydrochloric acid, and the residue is found to contain small diamonds, some of which are colourless, others are black (called carbonado). A portion of the residue is also in the form of graphite.

Later experiments by Sir Charles Parsons and others indicate, however, that the formation of the diamonds is due to the retention of carbon monoxide by the iron, and not the production of high pressure.

395. Graphite.—Graphite (Greek *grapho* = I write) occurs naturally, and is still obtained in Cumberland for "black-lead" pencils. It is also called plumbago or black lead, probably because it marks paper like lead.

Graphite is now manufactured on a large scale at Niagara where cheap electric power is obtainable. The process consists of heating anthracite to a very high temperature by means of a powerful electric current. The method, which is due to Acheson, yields very pure graphite.

396. Properties of Graphite.—Graphite is (unlike diamond) a good conductor of heat and electricity, and for this reason is used very extensively for electrodes. It is a soft, dark grey substance with an almost metallic lustre, and a specific gravity of 2·2. Crystalline graphite occurs in six-sided crystals. It marks paper, and is therefore used in the manufacture of lead pencils. Graphite is very infusible, and on this account is largely used in the manufacture of "plumbago" crucibles. It is also used as a lubricant for machinery and for polishing gunpowder. When strongly heated in oxygen graphite burns with formation of carbon dioxide; the ash which is left consists of silica, SiO_2, ferric oxide, Fe_2O_3, and alumina, Al_2O_3. Graphite is oxidised, when gently heated with a mixture of potassium chlorate and nitric acid, to graphitic acid whilst diamond is unattacked.

397. Amorphous Carbon.—Amorphous carbon is familiar to us as charcoal, soot or lamp-black, animal charcoal or bone-black, and gas-carbon, all of which are more or less impure forms of carbon.

398. Charcoal.—Charcoal may be obtained by strongly heating wood or many other organic bodies in vessels from which air is excluded; or by the action of dehydrating substances, such as strong sulphuric acid, on these bodies.

Exp. 99.—Heat a few pieces of wood in a hard glass tube over the flame of a Bunsen burner. Volatile vapours are at first given off and burn at the mouth of the tube; when these are no longer to be seen, throw out the contents of the tube into water. The black charred product is wood charcoal.

Exp. 100.—Make about 20 grm. of sugar into a thick syrup by dissolving it in a little hot water, and place it in a deep glass cylinder; allow to cool; then pour in about 20 c.cm. of concentrated sulphuric acid. Presently the liquid will froth and blacken considerably, and a mass of black charcoal much more bulky than the sugar originally taken will be formed. Wash this thoroughly with water till free from acid, and there remains carbon in a granular amorphous condition.

Where wood is scarce, charcoal is prepared from it by distillation, as already mentioned; but where it is plentiful and waste is not important, the logs are arranged in heaps, covered with sods or earth to allow only a small supply of air, and then slowly burned.

399. Properties of Charcoal.—The chemical composition and properties of charcoal vary considerably with the kind of wood used and the temperature at which it is charred. When charred at a low temperature the charcoal is soft and light in colour, and it burns easily; it also contains a lower percentage of carbon than when charred at a high temperature. Thus a specimen of wood charred at a temperature of about 300° C. contained 70 per cent. of carbon and 4·5 per cent. of hydrogen, while when charred at a full white heat it contained 96 per cent. of carbon and 0·5 per cent. of hydrogen.

Wood charcoal has a specific gravity of about 1·5; yet when dry it floats on water. This is explained when a piece of charcoal is placed on water under the receiver of an air pump: as the pump is worked, air escapes from the charcoal and it gradually sinks. The charcoal is porous, and the air contained in its pores reduces its apparent specific gravity to about 0·2, the specific gravity of air being only about 0·0013 (water = 1). Charcoal also absorbs other gases to a varying extent.

Cocoa-nut charcoal, under favourable conditions, was found to absorb of—

Ammonia...	...	...	172	times its volume.
Hydrochloric acid		...	165	,, ,, ,,
Nitrous oxide	...	....	99	,, ,, ,,
Carbon dioxide	...	...	97	,, ,, ,,

On the other hand, charcoal only absorbs slightly more than its own volume of hydrogen.

Exp. 101.—Fill a test-tube with dry ammonia gas by displacement, and stand it over mercury in a trough. Heat a small piece of charcoal red hot in the crucible tongs, and plunge it, while still glowing, under the mercury; then allow it to rise into the test-tube. The mercury rises in the tube as the ammonia is rapidly absorbed by the charcoal.

This property of charcoal is used in deodorising and disinfecting sewers and hospital wards. The charcoal not only absorbs gases and the effluvia evolved by putrefying matter, but also rapidly oxidises them by means of the oxygen already present in its pores: this oxygen is more active than ordinary gaseous oxygen, and is even capable of killing bacteria.

Exp. 102.—Mix a little finely-powdered wood charcoal with water, and pour the whole on to a filter paper in a funnel. Pour some sulphuretted hydrogen water through the charcoal and test the filtrate by lead acetate solution. No black precipitate of lead sulphide is formed, showing that the sulphuretted hydrogen has been oxidised by the oxygen absorbed in the charcoal.

Charcoal also possesses the power of decolorising liquids; for this purpose animal charcoal is more generally used (see § 402).

Charcoal burns in air without flame or smoke, unless it has been prepared at a low temperature and is therefore very impure; in excess of air carbon dioxide (CO_2) is produced, but in a limited supply of air carbon monoxide (CO) is formed.

400. Reducing Action of Charcoal.—On account of the ease with which it combines with oxygen, charcoal (and other forms of amorphous carbon) acts as a strong reducing agent at high temperatures.

We have already had an example of a *gaseous* reducing agent in hydrogen, which, owing to its affinity for oxygen, reduces many oxides to the metallic condition. Also in

sulphurous acid or phosphorous acid we have instances of *liquids* as reducing agents, their activity being due to the ease with which they undergo oxidation to sulphuric acid and phosphoric acid respectively. In carbon we have a *solid* reducing agent which finds very frequent employment in operations conducted at high temperatures, the carbon under such conditions being oxidised to carbon monoxide or dioxide at the expense of the oxygen contained in the bodies with which it is mixed.

Thus, most metallurgical operations involving a reduction of oxides to the metal are carried out with the use of carbon in the form of coke or coal, which is oxidised to CO or CO_2 in the process.

Exp. 103.—Make an intimate mixture of about a gramme of finely-powdered oxide of lead (litharge) with about one-tenth its weight of charcoal, and heat to redness in a hard glass tube or porcelain crucible for five minutes. Now throw some of the powder into a mortar with a little water and rub it up, using pressure, with the pestle, and then wash away the charcoal by means of a stream of water. Pellets or plates of metallic lead will be obtained—

$$2\,PbO + C = 2\,Pb + CO_2.$$

Similarly, oxide of copper or bismuth may be reduced, and metallic copper or bismuth obtained from them.

The reduction of iron ores, or oxide of zinc or tin, are examples of similar reductions carried out on the large scale.

401. Preparation of Pure Charcoal.—*Pure* charcoal may be prepared by dehydrating pure cane-sugar as in Exp. 100, and heating it in a current of chlorine, when any hydrogen present is removed as hydrochloric acid, and finally heating in a current of hydrogen. Instead of proceeding as in Exp. 100, the cane-sugar may be heated in a platinum crucible when water is driven off; the product is then treated with chlorine and hydrogen as before.

402. Animal Charcoal, or Bone Black.—Another kind of charcoal is made by heating bones in closed iron retorts. It is a very porous mixture of charcoal with the mineral constituents of the bones, chiefly calcium phosphate. It is used

for decolorising raw sugar, as it has the property already referred to of removing many colouring matters from solution.

Exp. 104.—Shake up with animal charcoal a hot solution of indigo or litmus for a few moments and then pour it on a filter; the filtrate will be colourless. That the colouring matter is removed by the animal charcoal and not by the filter, may be shown by pouring a similar solution, which has not been treated by animal charcoal, through a filter paper.

403. Lamp-black.—Lamp-black may be made by burning resin or turpentine, and bringing a cool surface, *e.g.* the under-side of a porcelain basin filled with cold water, into the flame. In this form, after treatment with chlorine, a particularly pure and finely-divided form of carbon is prepared. Lamp-black is used in making paint and for printers' ink.

404. Gas-carbon and Coke.—Two forms of amorphous carbon are obtained by the destructive distillation* of coal (see §§ 430, 431), namely, *gas-carbon* and *coke*. The former is nearly pure carbon, but the latter contains all the non-volatile products present in the coal. Gas-carbon is very hard and has a specific gravity of 2·35. It is a good conductor of electricity, and is on this account used for making the carbon electrodes of arc lights.

405. In whatever form it occurs, carbon is infusible, but it volatises without fusion at the temperature of the electric furnace. It cannot be considered an element of great chemical activity, since at ordinary or moderate temperatures it does not combine directly with any of the elements except fluorine At high temperatures, however, carbon does unite directly with a considerable number of elements, *e.g.* oxygen, sulphur, hydrogen, nitrogen, iron, and aluminium.

406. Proof that the Allotropic Modifications of Carbon all Consist of the Same Element.—The best proof consists in showing that whichever allotropic modification is used, 12

* The process of *destructive distillation* consists in distilling a complex substance, such as wood or coal, out of contact with air.

parts by weight of it on combustion in oxygen yield 44 parts by weight of carbon dioxide. The experiment may be carried out in the following manner :—

A small quantity of any form of carbon (say graphite) is accurately weighed out in a porcelain "boat" C (Fig. 76); this is then introduced into one end of a hard glass tube, the greater part of which is filled with granulated copper oxide. The tube is closed at each end with a one-holed rubber cork through which passes a short glass tube. The end of the tube at which the boat is placed is connected with a supply of dry oxygen, the other end with a series of bulbs containing strong caustic potash solution. These bulbs, together with a calcium chloride tube A (the object of which is explained in § 293, where a similar experiment is described with sulphur), are weighed before being placed in position.

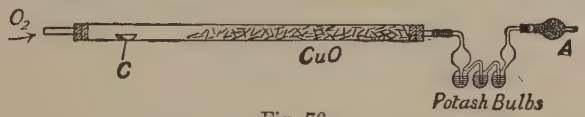


Fig. 76.

The tube is now heated in a furnace; at first only the burners under the copper oxide are lighted, but when this becomes red-hot the heating is extended to the boat and a slow current of oxygen is passed through the tube. The carbon burns to carbon dioxide, which passes on and is absorbed by the caustic potash. Any carbon monoxide which is at first formed owing to incomplete combustion is converted into carbon dioxide during its passage over the heated copper oxide.

When nothing remains in the boat but a trace of ash, and when bubbles of gas cease to be absorbed in the potash bulbs, the latter are disconnected, and after cooling are reweighed* (together with the calcium chloride tube). The increase in weight gives the weight of carbon dioxide formed. The boat is also allowed to cool and is reweighed. The difference

* A current of dry air is first passed through them to displace the oxygen.

between the final weight of the boat (which includes the weight of the ash) and the weight of the boat + graphite (previously determined) gives the actual weight of graphite burnt (*i.e.* the ash is allowed for).

Let W_1 = weight of boat + graphite.

W_2 = weight of boat + ash.

Then $W_1 - W_2$ = weight of graphite burnt.

Also let W_3 = weight of KOH bulbs + $CaCl_2$ tube before absorption,

and W_4 = weight of KOH bulbs + $CaCl_2$ tube after absorption.

Then $W_4 - W_3$ = weight of CO_2 formed.

It will then be found that whatever form of carbon is used the ratio $\frac{W_4 - W_3}{W_1 - W_2}$ is equal to $\frac{44}{12}$ or $\frac{11}{3}$.

407. Hydrocarbons.—These are compounds consisting of carbon and hydrogen alone. The direct combination of carbon and hydrogen in the laboratory can only be effected with difficulty (marsh gas, CH_4, and acetylene, C_2H_2, being formed), and yet the number of known hydrocarbons is exceedingly great.

They vary in physical and chemical character according to their composition, and according to the arrangement of the ultimate particles of carbon and hydrogen of which they are composed. Hydrocarbons containing a small number of atoms of carbon and hydrogen are usually gaseous, such as marsh gas, CH_4, ethylene, or olefiant gas, C_2H_4, acetylene, C_2H_2; and those whose composition is more complex are at ordinary temperatures liquid, such as pentane, C_5H_{12}, benzene, C_6H_6, turpentine, $C_{10}H_{16}$; or solid, such as naphthalene, $C_{10}H_8$, anthracene, $C_{14}H_{10}$.

The hydrocarbons may be arranged in homologous series in accordance with the relative numbers of atoms of carbon and hydrogen which they contain—

(1) The *Marsh Gas Series* (or Paraffins), the first member of which is marsh gas, CH_4, and succeeding members, C_2H_6, C_3H_8, and so on, the general expression for the relation of carbon to hydrogen being C_nH_{2n+2}.

(2) The *Ethylene Series* (or Olefines), the first member of which is ethylene, C_2H_4, and succeeding members, C_3H_6, C_4H_8, and so on, the general expression for the relation of carbon to hydrogen being C_nH_{2n}.

(3) The *Acetylene Series*, the first member of which is acetylene, C_2H_2, and succeeding members, C_3H_4, C_4H_6, and so on, the general expression for the relation of carbon to hydrogen being C_nH_{2n-2}.

(4) Hydrocarbons having the general formula C_nH_{2n-4} and C_nH_{2n-6}, and others having still smaller proportions of hydrogen, are known, a familiar example of the C_nH_{2n-6} series being benzene, C_6H_6, the first member of this series.

Only the three hydrocarbons, marsh gas, ethylene, and acetylene will be considered here.

Marsh Gas or Methane, CH_4.

408. Occurrence.—This gas is so called because it is frequently generated in marshes or pools where vegetable matter is in course of decay. The " blowers " in coal-mines discharge large quantities of this gas, which from its inflammable nature is termed " fire-damp," and it is also formed in the destructive distillation of wood or coal, coal gas containing usually about 35 per cent. of marsh gas.

409. Preparation.—When charcoal is heated in an atmosphere of hydrogen to a temperature of 1,200° C. a certain amount of chemical combination takes place, with formation of marsh gas. It is also produced, together with acetylene, when electric sparks are passed between carbon poles in an atmosphere of hydrogen.

Marsh gas is generally prepared in the laboratory by strongly heating a mixture of anhydrous sodium acetate and dry

soda-lime (lime which has been slaked by the addition of caustic soda solution)—

$$\underset{\text{Sodium acetate.}}{CH_3{\cdot}CO_2Na} + NaOH = Na_2CO_3 + CH_4.$$

Exp. 105.—Weigh out about 10 grm. of anhydrous sodium acetate and 30 grm. of soda-lime; intimately mix them in a mortar and dry by gently heating in a porcelain dish. Introduce the mixture into a small hard glass flask provided with a cork and delivery tube, and heat strongly. Collect the gas which is evolved over water at the pneumatic trough.

As thus prepared marsh gas is by no means pure; it is contaminated with ethylene, C_2H_4, and hydrogen. The former may be removed to a large extent by passing the gas through a wash-bottle containing strong sulphuric acid.

A purer gas may be obtained readily by the action of water on aluminium carbide—

$$Al_4C_3 + 12\ H_2O = 3\ CH_4 + 4\ Al(OH)_3.$$

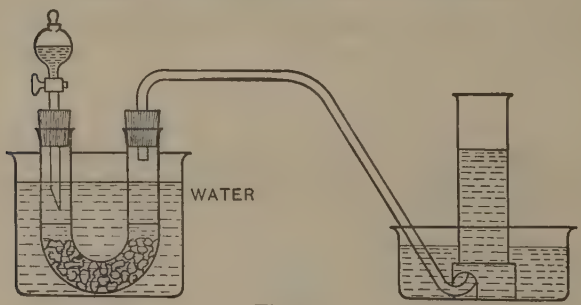


Fig. 77.

Pure marsh gas may be obtained by the action of nascent hydrogen on methyl iodide, CH_3I. The methyl iodide is dissolved in methyl alcohol and placed in the dropping funnel (see Fig. 77). The zinc copper couple is placed in the U-tube and covered with methyl alcohol to which two drops of dilute sulphuric acid are added. The methyl iodide is dropped from the funnel, and the methane produced is collected as shown, after the air has been displaced.

The reaction proceeds according to the equation—

$$CH_3OH + CH_3I + Zn = CH_4 + ZnI(OCH_3),$$

or we may write the equation—

$$CH_3I + \underset{\text{Nascent.}}{2\,H} = CH_4 + HI\,;$$

the nascent hydrogen is produced by the moist zinc-copper couple.

410. Properties.—Marsh gas or methane is a colourless and odourless gas, which condenses to a colourless liquid boiling at $-160°$ C. and freezing at $-184°$ C. It is only slightly soluble in water, 100 volumes of which at 0° C. dissolve 5·5 volumes of the gas. It burns with a pale blue non-luminous flame, forming carbon dioxide and water vapour—

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O.$$

It is a stable gas and is unaffected by chemical agents such as strong nitric acid, sulphuric acid, alkaline permanganate, etc.

With oxygen or air within certain limits it forms an explosive mixture, and the explosions occurring in coal-mines are usually due to the firing of such a mixture. With the halogen elements* it forms compounds in which part or even the whole of the hydrogen is replaced atom for atom by these elements ; this process is known as *substitution*, and the compounds produced are called *substitution products* as already mentioned in § 156. Thus when equal volumes of chlorine and marsh gas are mixed in *diffused daylight*, they gradually react with formation of methyl chloride, CH_3Cl, and hydrochloric acid—

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

If more chlorine is present it gradually replaces the remaining hydrogen till finally the whole of the hydrogen is removed—

* *Iodine* does not act directly on marsh gas except in the presence of a substance such as iodic acid, which destroys the HI as soon as it is formed, and so prevents it from exercising a reducing action on the substitution product formed, with re-formation of CH_4.

$$CH_3Cl + Cl_2 = \underset{\text{Metbylene chloride.}}{CH_2Cl_2} + HCl.$$

$$CH_2Cl_2 + Cl_2 = \underset{\text{Chloroform.}}{CHCl_3} + HCl.$$

$$CHCl_3 + Cl_2 = \underset{\text{Carbon tetrachloride.}}{CCl_4} + HCl.$$

On mixing chlorine and marsh gas in direct sunlight an explosion occurs with separation of carbon—

$$CH_4 + 2\,Cl_2 = C + 4\,HCl.$$

411. Composition of Marsh Gas.—This may be determined by exploding a known volume (say 30 c.cm.) with an excess of oxygen (120 c.cm.) in a eudiometer; the carbon and hydrogen unite with oxygen to form carbon dioxide and water vapour respectively. A diminution* of 60 c.cm. will be recorded. Carbon dioxide and the excess of oxygen remain, and the amount of the former may be found by absorbing it with caustic potash; this will give a reduction of 30 c.cm., the oxygen excess being 60 c.cm. Expressing this shortly,

2 vol. marsh gas + 8 vol. oxygen = 4 vol. water vapour + 2 vol. carbon dioxide + 4 vol. oxygen.

Now water vapour contains its own volume of hydrogen, and two volumes of marsh gas therefore consist of four volumes of hydrogen, and that amount of carbon which is contained in two volumes of carbon dioxide, *i.e.* one atom. This would give us the composition CH_4.

We find, by weighing, that the density of marsh gas as compared with hydrogen is 8, so that its molecular weight must be 16: this agrees with the formula CH_4, for $C = 12$, $H_4 = 4 \times 1$, and $12 + 4 = 16$.

Ethylene or Olefiant Gas, C_2H_4.

Ethylene is the first member of the *olefine* series of hydrocarbons. It occurs as one of the products of the destructive distillation of coal, and the luminosity of the coal gas flame is largely owing to its presence.

* When the water vapour has condensed.

412. Preparation.—Ethylene is prepared by heating a mixture of alcohol, C_2H_5OH, and excess of sulphuric acid. Alcohol behaves towards sulphuric acid just like caustic potash does, *i.e.* it forms a salt with elimination of water—

$$K{\cdot}OH + H_2SO_4 = KHSO_4 + H_2O.$$

$$C_2H_5{\cdot}OH + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5{\cdot}HSO_4} + H_2O.$$

The group of elements C_2H_5 is called *ethyl*, and plays the part of a metal.

When ethyl hydrogen sulphate is heated, however, it decomposes with formation of ethylene and sulphuric acid—

$$C_2H_5{\cdot}HSO_4 = C_2H_4 + H_2SO_4.$$

The last two equations represent, therefore, the two stages of the reaction which takes place in the preparation of ethylene.

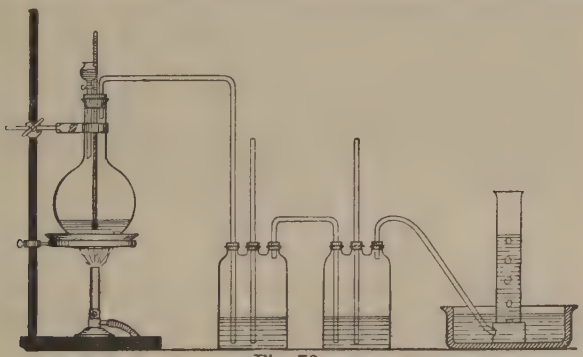


Fig. 78.

Exp. 106.—Mix together 200 c.cm. of sulphuric acid and 50 c.cm. of water, and cautiously add 50 c.cm. of alcohol. Pour into a wide-mouthed flask of about a litre capacity, fitted with a cork through which pass (1) a rather wide delivery tube, (2) a thermometer *dipping into the liquid*, (3) a dropping funnel (see Fig. 78). Heat until the temperature rises to 165° C. and keep as near this as possible. If the alcohol is impure a good deal of frothing occurs, which is, however, less troublesome if sand has been introduced into the flask. The gas should be passed through wash-bottles containing a solution of caustic soda to absorb carbon dioxide and sulphur dioxide, and collected over water, but the

first three or four cylinders of it should be rejected, as they contain a very explosive mixture of ethylene and the air displaced from the flask and wash-bottles.

Syrupy phosphoric acid of such a concentration that it boils at 200° C. may with advantage be substituted for sulphuric acid. When this is used the frothing and charring are avoided, and, CO_2 and SO_2 being absent, the washing of the gas may be dispensed with.

413. Properties.—Ethylene is a colourless gas which is freely soluble in alcohol, but only slightly soluble in water, 100 volumes of water dissolving about 25·6 volumes of the gas at 0° C. It is more easily condensed to the liquid form than marsh gas; the liquid boils at — 103° C. and freezes at — 169° C. The gas burns with a luminous flame, which is smoky unless it is diluted with hydrogen or marsh gas. It combines directly with chlorine to form an oily liquid, Dutch liquid or ethylene dichloride, $C_2H_4Cl_2$; hence the name *olefiant* (or oil-forming) gas.

One molecule of ethylene also combines directly with one molecule of each of the following—bromine, iodine, hydrobromic acid, hydriodic acid, sulphuric acid, and with two atoms of nascent hydrogen.

On account of this property of forming *addition* compounds, ethylene is said to be *unsaturated*; marsh gas, which only forms *substitution* compounds, is said to be *saturated*. It combines with sulphur dichloride to form mustard gas—

$$2\,C_2H_4 + SCl_2 = S(C_2H_4Cl)_2.$$

With oxygen ethylene explodes on ignition much more powerfully than marsh gas, and great care must be exercised in dealing with mixtures of ethylene with air or oxygen.

$$\underset{1\text{ vol.}}{C_2H_4} + \underset{3\text{ vols.}}{3\,O_2} = \underset{2\text{ vols.}}{2\,CO_2} + 2\,H_2O.$$

The composition of ethylene is established by a similar method to that employed in the case of marsh gas.

Acetylene, C_2H_2.

Acetylene is the first member of the acetylene series of hydrocarbons. It occurs in small quantity in coal gas, and is formed when coal gas is burnt with an insufficient supply

of air, or when the flame is cooled by impinging on a cold surface. It is also formed when ethylene is passed through a red-hot tube. Carbon and hydrogen unite directly to form acetylene when a powerful electric discharge is passed between carbon poles in an atmosphere of hydrogen.

414. Preparation.—The most convenient mode of preparation consists in treating calcium carbide, CaC_2 (a grey solid obtained by heating lime or limestone and coke in an electric furnace), with water—

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2.$$

Exp. 107.—Place a small lump of calcium carbide under a cylinder of water inverted in a trough of water. Acetylene is formed without heating and rises up into the cylinder.

Prepared in this way it has an objectionable smell due to traces of phosphoretted hydrogen (formed by the action of water on the calcium phosphide present), but it can be obtained fairly pure by passing the gas through a wash-bottle of copper sulphate solution, then through a "tower" containing chloride of lime. The presence of acetylene in coal gas which is burning in an insufficient supply of air can be shown by the following experiment.

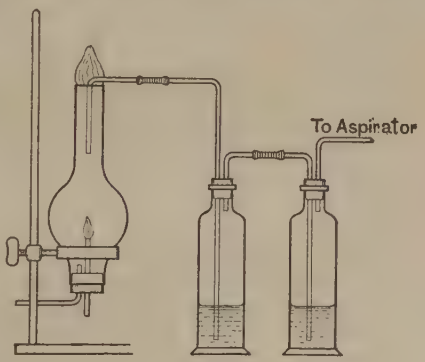


Fig. 79.

Exp. 108.—Fit into an ordinary lamp-chimney a cork through which passes a short piece of straight wide tubing, and a second narrow piece bent at right angles, as shown in Fig. 79, and connected with the supply of coal gas. Close the aperture at the top of the chimney, and allow the gas to escape by the straight tube until the air is displaced; then light it at the lower extremity of this tube and uncover the aperture at

the top of the chimney. The flame will then pass up the tube and attach itself to the inner opening where the air and coal gas meet, the flame area being air and the surrounding atmosphere being coal gas.

The gas escaping at the top of the chimney may be ignited, and here we shall have a flame of coal gas burning in air as in combustion under ordinary circumstances. In the flame burning in coal gas at the base of the chimney much acetylene is formed, and if a glass tube is passed through the upper flame and gas is aspirated from the inside of the lamp glass through an ammoniacal solution of cuprous chloride, cuprous acetylide, Cu_2C_2, will be formed, from which pure acetylene can be obtained (see § 415).

415. Properties.—Acetylene is a colourless gas which has a sweetish smell when pure. It is poisonous.

Water dissolves its own volume of the gas at ordinary temperatures, and it may be condensed to a liquid boiling at — 81° C. and freezing at — 84° C. It burns with a luminous smoky flame, and forms very explosive mixtures with air or oxygen. Acetylene is soluble in acetone, which under a pressure of 12 atmospheres dissolves 300 volumes of the gas at ordinary temperatures; and the gas is generally stored in this way.

By using a burner with a very fine hole, the flame of acetylene becomes non-smoky and exceedingly luminous. As might be expected, the gas is employed to a considerable extent for illuminating purposes, *e.g.* in bicycle lamps, and for house illumination where coal gas is not available; it is generated as required by the action of water on calcium carbide, for it cannot safely be stored under pressure on account of its tendency to explode when compressed. Acetylene is also used to increase the luminosity of other gases, such as oil gas. Acetylene is used extensively for oxy-acetylene welding. A mixture of acetylene (from an acetone solution) and oxygen is burnt in a special blowpipe and the flame reaches a temperature of 3000° C.

Acetylene behaves like an acid, as it has replaceable hydrogen. Thus if acetylene is passed into an ammoniacal solution of cuprous chloride a red precipitate, cuprous acetylide, Cu_2C_2, is formed—

$$Cu_2Cl_2 + C_2H_2 = Cu_2C_2 + 2\,HCl.$$

Silver and sodium acetylides are easily prepared. The copper and the silver compounds are explosive.

By the action of hydrochloric acid on cuprous acetylide pure acetylene is obtained—

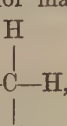
$$Cu_2C_2 + 2\,HCl = C_2H_2 + Cu_2Cl_2.$$

Acetylene combines *directly* with either *one* or *two* molecules of chlorine or bromine ; it is therefore more unsaturated than ethylene, which can only take up *one* molecule of each of these elements. It also combines directly with the halogen acids and with nascent hydrogen.

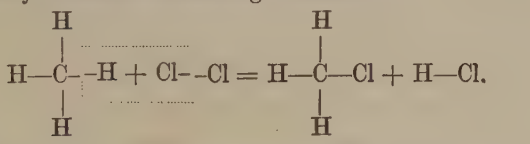
Acetylene when passed into dilute sulphuric acid in which mercuric oxide is suspended adds on the elements of water and forms *acetaldehyde*, which is used for the preparation of acetic acid, etc.—

$$C_2H_2 + H_2O \xrightarrow[HgO]{} CH_3CHO.$$

416. Constitution of Marsh Gas, Ethylene, and Acetylene. —The only possible formula for marsh gas, assuming that hydrogen is monovalent, is

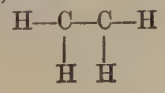


which makes carbon tetravalent. When chlorine acts on marsh gas the hydrogen atoms are gradually replaced by chlorine, as we have seen, the valency of carbon remaining the same—

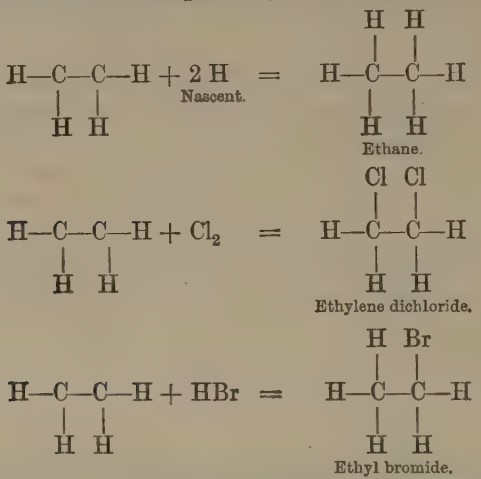


and so on.

Now when we try to represent ethylene by a constitutional formula in which carbon is tetravalent and hydrogen monovalent, we find we cannot do it ; the nearest we can get is to make carbon *trivalent*, thus—



Clearly, then, carbon is not exerting its full valency, and we should expect that it would easily be able to take up two monovalent atoms and so make both carbon atoms tetravalent. This we have already found to be the case, and the following equations express the action of nascent hydrogen, chlorine, and hydrobromic acid respectively on ethylene :—

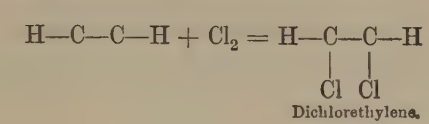


Ethylene is unsaturated, but the compounds ethane, ethylene dichloride, and ethyl bromide, produced from it by addition, are saturated; they cannot take up any more atoms because the two carbon atoms are now exerting their full valency.

On trying to write a formula for acetylene we find that the carbon can only be represented as divalent (keeping hydrogen monovalent) thus— H—C—C—H.

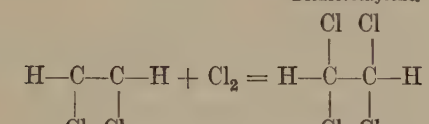
There are, therefore, *four* free carbon valencies to satisfy and acetylene should be able to take up four monovalent atoms, which we have already seen to be the case. Intermediate compounds which are still unsaturated are, however, formed by adding on two monovalent atoms. Thus with chlorine we have—

1st Stage.



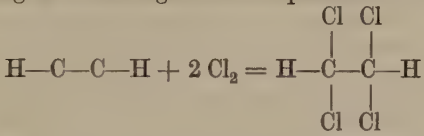
Dichlorethylene.

2nd Stage.

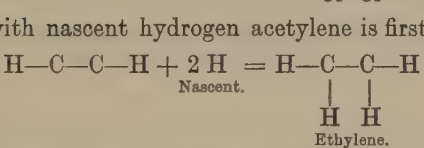


Tetrachlorethane.

Or, writing the two stages in one equation—



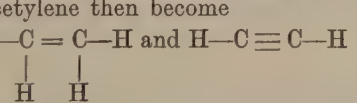
Again, with nascent hydrogen acetylene is first reduced to ethylene—



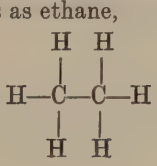
Ethylene.

and the ethylene is then reduced to ethane, according to the equation already given.

It is customary to represent carbon as tetravalent in unsaturated compounds, as well as in saturated compounds, by putting one or two extra bonds between the carbon atoms; ethylene and acetylene then become



respectively. It must not be supposed by this that the carbon atoms are more firmly united together in these compounds than in such substances as ethane,



in which the carbon atoms are only united by one bond; on the contrary, they are *much less firmly* united.

Fuels.

Fuels can conveniently be grouped as follows :—Solid, Liquid, and Gaseous. Each of these will be discussed separately in the following pages.

417. Solid Fuels.—The most important solid fuels are coal, lignite, peat, and wood. Coal is the result of the decay of vegetation. In the successive stages in this change hydrogen and oxygen are eliminated, and the proportion of carbon increases. Thus peat, lignite, bituminous coal, and anthracite may be considered as successive stages in the formation of coal. If the following table is considered it will readily be seen, that the carbon content increases and the other contents decrease as we pass from peat to anthracite.

PERCENTAGE COMPOSITION OF SOLID FUELS.

Solid Fuels.	C.	H.	N.	O.
Wood	50	6	1	43
Peat	58	5	2	35
Lignite	73	5	1	21
Bituminous coal ...	85	5	1	9
Anthracite	93	3	1	3

418. Peat.—Peat is formed where plants undergo decay and form accumulations. As a fuel, peat is not of great value on account of the large water content, which it holds so firmly. Various methods are adopted for drying peat, and an electrical process has been suggested.

419. Lignite.—In deposits of peat and the remains of vegetation which have lain for long periods of time, the process of parting with the more volatile constituents and consequent

increase in the proportion of carbon goes on, and instead of peat we have a much denser product known as *brown coal* or *lignite*, in which the structure of the vegetation composing it can, however, still be observed. Lignite varies greatly in composition, especially in regard to the amount of moisture and ash, and is a low grade fuel.

420. Bituminous Coal.—In the older formation of the earth's crust there are large deposits of *coal*, which have resulted from long-continued action similar to the foregoing. The seams of coal usually occur at some depth, and are overlaid by other strata. The vegetable tissue from which coal is derived has thus been subjected to immense pressure and to increased temperature, and under these agencies, acting over long periods of time, the changes already noticed in the passage from woody tissue to lignite have been still further accentuated. Bituminous coal is darker in colour, denser, and more brittle than lignite. It gives large quantities of volatile matter on distillation, and is used in the manufacture of coal gas and for open fires.

421. Anthracite.—Anthracite is a "smokeless" form of coal. It is a hard coal and is used for special purposes, *e.g.* steamships, stoves in houses, etc.

422. Wood.—Wood consists of the partially dried and hardened tissue of trees and bushes. As a fuel it is not particularly economical, but it is used fairly extensively for the following reasons:—

(i) It is readily inflammable.

(ii) It gives a good flame on burning and leaves a small amount of ash and soot.

However, the maximum temperature that can be obtained with wood is comparatively low compared with other fuels.

423. Action of Heat on Wood.—When wood is heated in the air it chars, gives off inflammable gases, and burns, leaving a black mass of charcoal, which slowly burns away.

By the distillation of wood in absence of air we obtain wood gas, a watery distillate, wood tar, and charcoal. *Wood gas* is used for illuminating purposes in Germany and Switzerland. The temperature of distillation must be very high, however, or the gas does not contain sufficient illuminating gases (heavy hydrocarbons) to be of any use for lighting purposes. The high temperature decomposes a large quantity of liquid oils which would simply distil over if a lower temperature were used. This decomposition is helped by the use of cast-iron retorts instead of clay retorts.

The composition of wood gas as used for illuminating purposes varies between the following wide limits :—

Hydrogen	18 to 42	per cent.
Marsh gas	9 to 35	,,
Carbon monoxide	22 to 62	,,
Ethylene, etc.	9 to 35	,,

Practically no sulphur compounds are produced, but a considerable amount of carbon dioxide is given off, which is removed by slaked lime as in the case of coal gas.

The watery distillate contains only a small quantity of ammonia, but a number of organic substances are prepared from it, of which the chief are wood vinegar (acetic acid), wood spirit (methyl alcohol), and acetone.

Wood tar contains many organic substances, of which creosote is the most important; the latter is used for the preservation of timber.

The residue left in the retort after the distillation is *wood charcoal*, which has already been described.

424. Liquid Fuels.—The most important of the liquid fuels is petroleum, which varies considerably in composition according to the part of the world where it occurs. Thus American petroleum mainly consists of *paraffins*. Russian petroleum is mainly *ethylenes*, and Borneo petroleum contains a large percentage of aromatic hydrocarbons.

425. Treatment of Mineral Oils.—The constituents of *petroleum* or *natural oil* have different boiling-points and may, therefore, be separated by distillation, the receiver being changed at intervals. The chief products are as follows :—

Petroleum ether (boiling-point 40°—70°), *gasoline* and *petrol* (boiling-point 70°—90°) ; these three fractions have a specific gravity 0·65—0·70 ; they are too inflammable for use as illuminants, but are employed as solvents for resins and oils in the manufacture of lacquers and varnishes and for the production of explosive mixtures in gas engines.

Benzine or *benzoline* (boiling-point 90°—120° ; specific gravity 0·70—0·74) is used for dissolving oils and greases and for small lamps ; this fraction is also called *ligroin*.

Cleaning oil (boiling-point 120°—170°) is used for the purpose which its name implies, and also instead of turpentine in making varnishes.

Kerosene or *paraffin oil* (boiling-point 150°—300°) is used for illuminating and heating purposes.

The portion which distils over above 300° C. is partly liquid and partly solid at ordinary temperature. The liquid part is called *lubricating oil* and is used for lubrication. The solid is *paraffin wax*. It is separated from any adhering liquid by means of filter presses, and used in the manufacture of candles, night-lights, etc.

Vaseline is the residue which remains when some of the American petroleums are distilled *in vacuo* at low temperatures.

The oils obtained by distillation are generally free from sulphur, but are dark in colour. They are refined by agitation with sulphuric acid, followed by treatment with dilute caustic soda solution, by which means they are rendered nearly colourless and fit for use in lamps.

Shale oil is obtained by distilling *oil shale*, a bituminous shale found in large quantities in the coal measures in Mid-Lothian. The shale is broken up into small fragments and heated in vertical retorts, and the products of the distillation are passed through a condensing apparatus consisting of a long series of pipes, the arrangement being similar to that used in the manufacture of coal gas ; the distillation is assisted by passing steam in at the base of the retorts. The liquid

products collect in two layers, the lower consisting of an aqueous solution of ammonia and other substances, and the upper of oil and tar. The latter is a greenish brown mixture closely resembling petroleum, and on fractional distillation it yields a number of products which are very similar to those obtained from petroleum.

426. Alcohol and Methylated Spirit.—These are prepared by fermentation from potatoes, malt, and other vegetable substances, and are used fairly extensively for fuel and solvent purposes.

427. Gaseous Fuels.—The chief gaseous fuels are—

I. Natural Gas.
II. Coal Gas.
III. Producer Gas.
  (*a*) Air gas.
  (*b*) Water gas (and carburetted water gas).
  (*c*) Semi-water gas.

428. Natural Gas.—In certain localities, particularly Pennsylvania in the United States, a natural gas which consists largely of hydrocarbons has accumulated in cavities in the earth's crust, and when borings are made which reach to these cavities, the gas, which is under great pressure, rapidly rises to the surface. This gas is largely used for illuminating purposes.

429. Coal Gas and Wood Gas.—Before dealing with the manufacture of coal gas on the large scale it will be well to examine the action of heat on coal by experiment.

Exp. 109.—Examine a coal fire, or heat a small piece of coal in a gas flame. You will notice the softening of the coal where it is heated, the giving off of an inflammable gas, and the final burning of the coal. The coal also lights easily.

Exp. 110.—Take a jar of oxygen and lower into it a small piece of coal on a deflagrating spoon after lighting a corner. When the coal has stopped burning, test the contents of the jar for water by means of anhydrous copper sulphate and for carbon dioxide by lime water.

The products of combustion are thus seen to be carbon dioxide and steam.

Exp. 111.—Set up the apparatus shown in Fig. 80. A is a hard glass tube about 6 in. long. B is a wide test-tube. Before placing A in position half-fill it with dry coal dust, and shake to make an air space over the coal dust. Heat the tube carefully. Note the formation of smoke and brown fumes which condense to a liquid in B. This liquid separates out into two layers; the upper layer is an aqueous solution of various substances —*gas liquor*, the thick brown lower layer is *tar*. After some time apply a light to the gas escaping at C; it burns: this inflammable gas is *coal gas*. Test the gas with lead acetate paper; note the blackening, showing the presence of *sulphur* compounds in the gas. When the gas has stopped coming off break the tube A and note the hard *coke*.

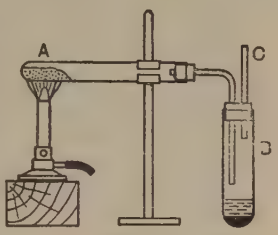


Fig. 80.

430. Manufacture of Coal Gas.—This experiment is repeated on the large scale in the manufacture of coal gas. This process requires the use of special plant, which may be described in outline as follows :—

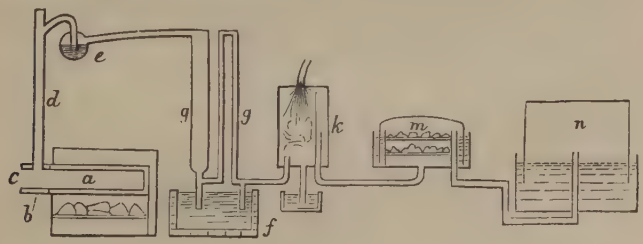


Fig. 81.

The coal is heated in horizontal tubular fireclay *retorts*, *a*, (Fig. 81), somewhat ⌓ shaped in section and six or more feet long. The open end of the retort is tightly attached to the iron furnace front *b*, which has for each retort a door *c*, through which coal can be shovelled in and coke removed, and also a vertical iron pipe, the *rising main d*, through which the gas

is driven by the decomposition. The retorts are generally arranged in groups of five for convenience of heating by a single furnace below each group, and are now generally tubular, with a door and rising main at each end.

In order to prevent the escape of gas during the charging of the retorts with coal, a curved pipe leads from the side of the rising main into a horizontal pipe, the *hydraulic main e.* This main contains condensed coal tar and water, below which the entering pipes dip, thus effectually sealing themselves against small changes of pressure. The level of the liquid in this main is kept constant by allowing any excess to flow off into the *tar pit f.*

The gas given off contains vapour of the tar and ammonia, and is too hot to be purified. It is now passed through a series of pipes, the *condensers g*, at first of large diameter to condense the tar, and later of smaller diameter to cool the gas for complete purification and to remove more tar. All the condensed liquids are collected in the tar pit, and separate into two layers, the lower the gas tar, and the upper an aqueous solution containing ammonia and ammonium salts, the *gas liquor.*

From the condensers the gas rises through a larger vessel full of coke, the *scrubber k*, in which it meets a fine spray of water, which removes all traces of ammonia. This liquid, together with the gas liquor from the tar pit, is mixed with sulphuric acid to expel sulphur gases and to recover the ammonia in the form of ammonium sulphate.

After leaving the scrubber the gas passes through three to six feet of slaked lime contained in the *purifiers m.* These are square gas-tight tanks sealed with water, and containing the slaked lime spread on wooden grids in layers about six inches deep. The gas passes through this lime, which absorbs sulphuretted hydrogen and carbon dioxide, and other sulphur compounds, forming a mixture of calcium sulphide, carbonate, etc., the *spent lime* or *gas lime.*

To remove as much as possible of the sulphur compounds, the gas is generally passed through ferric hydroxide contained in another purifier ; the ferric hydroxide is reduced to ferrous sulphide and sulphur is deposited. This mixture on being

exposed to the air becomes oxidised, and may be used again until the sulphur is present in too great excess. After leaving the purifiers the gas passes over into the *gas holders n*, where it is stored over water until it is required for use.

A ton of coal yields about 10,000 cub. ft. of coal gas, which varies in composition, but contains approximately—

Hydrogen	50 per cent.
Marsh gas	35 ,,
Carbon monoxide	8 ,,
Ethylene, etc.	5 ,,
Nitrogen and oxygen	3 ,,

Thus about 95 per cent. of the product has little or no illuminating power, this property being mostly due to the 5 per cent. of ethylene, etc.

Coal tar is a mixture of many organic substances which are separated by fractional distillation. Among the most important are benzene, naphthalene, anthracene, and phenol (carbolic acid).

431. Coke.—The residue in the retorts after the distillation of all the volatile products from coal is composed of two substances, *coke* and *gas-carbon*. The former is found in the centre of the retorts and consists principally of carbon, but contains all the non-volatile mineral matter present in the coal (*i.e.* the ash), and also small quantities of hydrogen, nitrogen, and oxygen; the latter occurs as a deposit on the roof and sides of the retorts and is nearly pure carbon. Gas-carbon has been sufficiently fully treated in § 404. We shall, however, study coke at somewhat greater length.

The amount of ash in coke varies with the coal used, but the average composition is—

Carbon	91·5 per cent.
Hydrogen	0·4 ,,
Nitrogen and oxygen	2·1 ,,
Ash	6·0 ,,

Exp. 112.—Try to light a piece of coke in a flame: it does not burn so readily as coal, and requires a higher temperature to set it on fire.

The temperature obtained by burning coke is very high, and, as there are no volatile products, there is generally neither luminous flame nor smoke from dry coke.

Blue flames are often noticed playing above a brightly burning coke fire: these are flames of carbon monoxide, formed by the reaction between carbon dioxide and red-hot carbon.

Coke is not only obtained as a by-product in the manufacture of coal gas, but it is also specially manufactured by heating coal to redness in coke ovens. The coke so prepared is very dense and is used in iron-smelting.

432. Producer Gas.—Producer gas is the name given to a gaseous fuel obtained from a solid fuel by a process of partial combustion, so that the gases obtained are combustible. The essential constituent of "producer gas" is carbon monoxide. The solid fuel employed is coal or coke, and the oxygen required for the combustion is obtained from the air, or from water, and in many cases from both air and water.

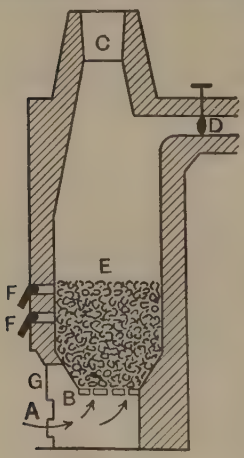


Fig. 82.

433. Air Gas.—Air gas is produced by sending an air blast through white hot coke or coal. The air is introduced at the bottom of a "Producer" A (Fig. 82) and oxidises the carbon to carbon dioxide mainly. As this passes up through the very hot fuel it is reduced to carbon monoxide—

$$C + O_2 = CO_2$$
$$CO_2 + C = 2\,CO.$$

The aim is to get the maximum amount of carbon monoxide, and the air supplied must *be insufficient* for the complete combustion of the carbon to carbon dioxide. A temperature of about 1000° C. is necessary for the complete reduction of the carbon dioxide, and as, at this high temperature, clinkering is likely to cause trouble, limestone is added which

forms a liquid slag and can thus be drawn off at intervals. The hot gas coming from the producer can be used directly for combustion, and hence both the heat of formation and the heat of combustion of the carbon monoxide are available—

$$2\,C + O_2 = 2\,CO + 58{,}000 \text{ cal.}$$

$$2\,CO + O_2 = 2\,CO_2 + 135{,}920 \text{ ,,}$$

The composition of air gas varies with the fuel used and the conditions. An average analysis can be given as—

CO	H_2	CH_4	CO_2	N_2
29	5	2	2	62 per cent.

36 per cent. combustible gases.

434. Water Gas.—It will be seen that in "air gas" there is a large proportion of nitrogen, and if steam is used instead of air this can be avoided. We may write the equation thus—

$$C + H_2O \text{ (steam)} = CO + H_2 - 29{,}000 \text{ cal.}$$

This reaction is strongly endothermic. As much heat would be required, water gas can only be made intermittently as follows :—Air is blown in first for five minutes, and the fuel by combustion is heated to the requisite temperature. This is called the "blow." The air gas obtained is used to produce steam which is then blown through the fuel for three minutes ("steam-blow," "cold blow," or "run"). When the temperature has fallen below a point such that the process is inefficient, air is again blown through the fuel.

However, this method has been modified so that the process is continuous. Thus it is arranged that during the "blow" a portion of the fuel is completely burnt to carbon dioxide and much heat is evolved. The temperature required is obtained quickly (one minute). Further, two "producers" are worked together, one being "blown" whilst the other is "run," and *vice versa*. Theoretically the composition of water gas should be 50 per cent. each of hydrogen and carbon monoxide, but an average analysis is as follows :—

H_2	CH_4	CO	CO_2	N_2
49	$\frac{1}{2}$	42		$4\frac{1}{2}$ per cent.

Water gas thus produced burns with a pale blue flame and is called "**Blue Water Gas,**" but if a luminous gas is required oil is sprayed into the fuel with the steam and **carburetted water gas** is obtained. Water gas has recently been used for the industrial prepartion of hydrogen (see § 79).

435. Semi-water Gas.—Semi-water gas is produced by passing a mixture of air and steam through red-hot coke or other fuel—

$$C + H_2O \rightarrow CO + H_2 - 29{,}000 \text{ cal.} \quad \ldots\ldots\ldots(1)$$

$$2\,C + O_2 \rightarrow 2\,CO + 58{,}000 \text{ cal.} \quad \ldots\ldots\ldots\ldots(2)$$

Equation (1) is endothermic, but equation (2) is exothermic. In actual practice the mixture of steam and air is arranged in such proportions that a convenient constant temperature is obtained in the producer. An average analysis of semi-water gas would give the following result :—

H_2	CH_4	CO	CO_2	N_2
14	3	27	4	52 per cent.

44 per cent. combustible gases.

The composition varies with the fuel used. Coal, unsuitable for boilers, etc., can be used as fuel, and in this way become a source of gaseous fuel.

436. Calorific Value of Fuels.—The *calorific* power of a fuel may be defined as the "amount of heat it will develop by the combustion of unit weight" (pound, gramme, kilogramme). The calorific power is found experimentally by burning the fuel electrically in a bomb calorimeter. The calorific power is generally measured in terms of the so-called *British Thermal Unit* (B.T.U.), *i.e.* the amount of heat required to raise one pound of water 1° F. (If 1° C. is used the unit is called the *pound calorie.*)

The calorific power shows the maximum amount of heat that can be developed under the most favourable conditions, and is thus not of great help to the practical man in buying fuels. The amount of ash, the type of furnace used, and the physical condition of the fuel all have to be considered.

Further, the "*calorific intensity*" or the maximum temperature that can be developed with the fuel under suitable conditions, has to be taken into account.

QUESTIONS.—CHAPTER XXII.

1. State what you know of the history of (*a*) carbon, (*b*) methane, (*c*) ethylene, (*d*) acetylene.

2. Show in tabular form the percentage of carbon and hydrogen in (*a*) wood, (*b*) peat, (*c*) lignite, (*d*) bituminous coal, (*e*) anthracite.

3. Taking the atmospheric pressure as 15 lb. on the square inch, calculate the weight of carbon in a column of the air whose base is a square mile, the carbon dioxide present being 0·06 per cent. by weight.

4. Compare the densities of diamond, graphite, and amorphous carbon. What do you regard as a full and sufficient proof that each of these bodies consists of the same element?

5. Describe how Moissan succeeded in preparing artificial diamonds.

6. How would you prove that sugar contains carbon?

7. How is wood charcoal manufactured? Describe experiments illustrating its chief properties.

8. What is animal charcoal, how is it prepared, and for what purpose is it used?

9. How would you show by experiment that a hydrocarbon contains carbon and hydrogen, and that it consists entirely of these elements?

10. Where is marsh gas found to occur naturally, and how is it usually drepared in the laboratory?

11. How can it be proved that the formula for marsh gas is CH_4?

12. Describe in detail the preparation of ethylene from alcohol.

13. Explain the terms—*substitution compound, addition compound, unsaturated compound, saturated compound.*

14. Describe with equations the chemical changes which take place when ethylene is burnt in air and in chlorine. How is ethylene distinguished from marsh gas?

15. Under what circumstances is acetylene formed during combustion of hydrocarbons? Suggest any means of determining the amount of acetylene in a mixture of hydrogen and acetylene?

16. How may acetylene be obtained in the pure condition? What are its chief properties, and for what purposes is it employed?

17. Describe how you would investigate experimentally the action of heat on coal in the absence of air,

18. Write a short account of the chief products of the destructive distillation of coal.

19. What are the chief products obtained from crude petroleum, and for what purposes are they employed ?

20. Briefly say what you know of the following :—air gas, water gas, semi-water gas ?

21. How is "producer gas" obtained? How would you show that it contains (*a*) CO ; (*b*) CO_2; (*c*) H_2?

22. Explain, with a sketch, the working of a "Producer."

23. 0·1931 grm. of diamond gave on complete combustion 0·704 grm. of carbon dioxide. Calculate the percentage of ash in the diamond (C = 12, O = 16).

24. What volume of ammonia will be absorbed by 10 grm. of charcoal if the density of the charcoal is 1·5 and if it absorbs 172 times its volume of the gas ?

25. 20 c.cm. of marsh gas are exploded with 50 c.cm. of oxygen. What will be the volume of the resulting gas ? Also what diminution in volume will take place on treating the resulting gas with excess of caustic potash ?

All volumes are supposed to be measured under standard conditions of temperature and pressure.

26. 30 c.cm. of ethylene are exploded with 150 c.cm. of oxygen and the resulting gas treated with excess of caustic soda. What volume of gas will remain and of what will it consist ?

All volumes are supposed to be measured at atmospheric temperature and pressure.

27. 10 c.cm. of acetylene measured at 120° C. and 750 mm. pressure are exploded with 80 c.cm. of oxygen measured at the same temperature and pressure. What will be the volume of the resulting gas if the temperature and pressure suffer no change and of what will it consist ?

28. Write a short account of Fuels. Define *calorific power*.

CHAPTER XXIII.

COMBUSTION.

437. Incandescence.—When the temperature of a body is raised to such a degree that it gives out light, it is said to be incandescent, or in a state of *incandescence*.

Exp. 113.—Take pieces of platinum wire, iron wire, magnesium ribbon, black lead, charcoal, and some iron filings. Heat the first five and drop the filings through a flame, holding the burner aslant. In each case light is given out.

Exp. 114.—Heat carefully about two grammes of ammonium dichromate in a porcelain basin, removing the flame as soon as a change takes place. Note that the change from red crystals to green powder is attended by incandescence.

Incandescence may thus be produced either by external heating or by the heat arising from chemical change.

Liquids and gases may also become so hot as to be incandescent, as in the flash seen during the explosion of a mixture of hydrogen and oxygen. The most common example of the incandescence of gases is afforded by flames.

438. Flame.—Whenever a gas or vapour is brought into an atmosphere with which it can react chemically, and the heat generated is sufficient to bring about incandescence of the particles, flame is produced. The heat is generated and the incandescence effected in the region where the reaction is carried on, that is, at the surface where contact occurs between the two gases, as is seen when a jar of hydrogen burns mouth downwards. When we speak of hydrogen and coal gas as being combustible gases, and of air as being a supporter of combustion, we imply that hydrogen and coal gas, when once ignited, burn in air. In ordinary flames this is the case; we have seen, however, in Exp. 108, that a jet of air can be made to burn in an atmosphere of coal gas.

In either case the flame marks the surface of contact between the air and the coal gas, and is the region where the chemical changes take place which transform the hydrogen and carbon of the coal gas into water and carbon dioxide as ultimate products.

Where the gases are intimately mixed and then ignited the burning takes place with great rapidity, and an explosion of a more or less violent nature ensues; but where a regular supply of the combustible product impinges upon the atmosphere in which it burns, a more or less steady flame is the result, the particular form of which is determined by the nature of the jet and the shaping influence of air-currents.

439. Point of Ignition.—In any case, before flame can be produced at all, the temperature of the combustible body must first reach a certain limit known as the *point of ignition*. This temperature varies with different bodies: the vapour of carbon disulphide may be ignited by a glass rod heated only to 150° C., whilst for hydrogen or coal gas a dull red heat (600° C.) is insufficient.

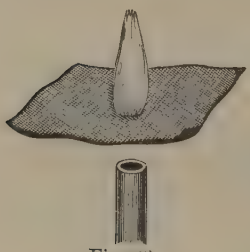


Fig. 83.

Exp. 115.—Place in small basins or little tin saucers two or three drops of benzoline, a few drops of paraffin, and a small piece of paraffin wax, and apply a light to each. The benzoline burns at once, the paraffin oil must be slightly warmed, while the paraffin wax must be heated over a burner before it will light. In these cases the temperature of ignition is called the *flash point*.

Conversely, a flame is extinguished if its temperature is by any means reduced below the point of ignition of the vapours consumed in it.

Exp. 116.—Hold a piece of wire gauze (about thirty meshes to the inch) horizontally over a Bunsen burner and about an inch above the orifice (Fig. 83). Turn on the gas and light it on the upper side of the gauze. The flame will not be communicated to the stream of gas on the under side of the gauze.

This is explained by the fact that the metal of the wire gauze is a good conductor of heat. The heat received from

the flame is rapidly conducted away by the gauze and dissipated, chiefly by radiation. This continuous loss of heat prevents the temperature of the gauze from reaching the ignition point of the gas, and, as the gas below the gauze can only become heated by contact with the gauze, it does not become ignited.

Exp. 117.—Make a piece of the wire gauze into a cylindrical roll, and place a candle within it. Now direct the flame of a Bunsen burner against the outer surface of the gauze ; the wax may be melted, but the candle cannot be lighted unless the gauze is heated to redness. The reason for this will be gathered from the explanation given in the previous experiment.

The *Davy Lamp* (Fig. 84) is a similar arrangement, in which an oil lamp is shut in by a layer of gauze ; and, even if such a lamp be entirely surrounded with inflammable gas, this will not become ignited, although the inflammable gas which passes through the gauze may burn inside it and fill the space above the oil lamp with flame. If, however, the gauze becomes strongly heated, or if the flame should be mechanically driven through the meshes, communication with the inflammable atmosphere outside may be established, and ignition will then take place.

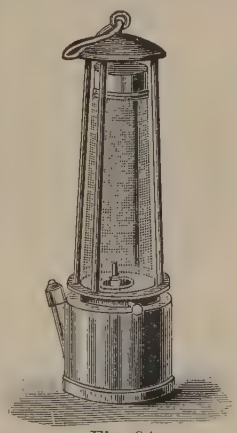


Fig. 84.

440. The Candle Flame. — The inflammable matter in a candle is the wax or tallow, consisting of compounds containing carbon and hydrogen. The wax is melted and passes up into the wick, which serves as a still supplying the vapours of carbon compounds to the space immediately surrounding it. That such a space exists containing combustible vapours may easily be shown by the following experiment :—

Exp. 118.—Depress a sheet of stout paper quickly into a candle flame to the level of the top of the wick, and hold it steadily there for about a second. On withdrawing it, a ring of sooty deposit will be

seen, and within it a clear space. Secondly, take a glass siphon-tube as shown in Fig. 85, and bring the shorter limb into the centre of the flame; presently the yellowish-brown vapours will be seen to pass down the tube and issue at the other end. These vapours will be found to be inflammable, and may be burnt at the end of the tube.

We can distinguish in the candle flame—

(1) The central zone surrounding the wick, and containing vapours of carbon compounds—the zone of no combustion (A in Fig. 85);

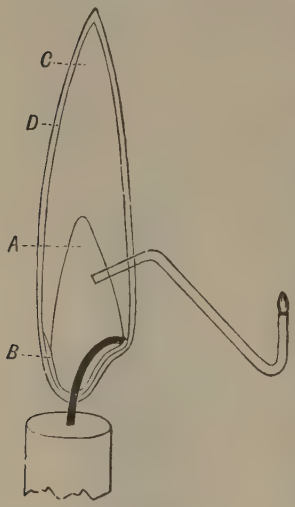


Fig. 85.

(2) The blue non-luminous zone, B, at the base;

(3) The luminous zone, C, surrounding the dark central zone; and

(4) The faintly luminous mantle D. Under ordinary circumstances this zone is not easily seen, but if a little finely-powdered common salt is sprinkled over the flame, it will flash out as a golden-yellow fringe, the colour of which is due to the salt.

The mantle can also be seen as a golden band above the wick by looking just above the glowing tip of the wick projecting through the side of the flame.

The changes which take place in the different zones are somewhat as follows:—(A) Vaporisation of the carbon compounds. As these pass up this zone decomposition takes place, with gradual formation of acetylene, and from it of dense hydrocarbons, and finally of free carbon particles, (B) The hydrocarbons present undergo partial combustion. with formation of carbon monoxide, hydrogen, and water—

$$CH_4 + O_2 = CO + H_2 + H_2O$$

$$C_2H_4 + O_2 = 2\,CO + 2\,H_2.$$

(C) The changes which take place in this zone are very complex. The formation of dense hydrocarbons and separation of carbon particles is continued. Also incomplete combustion takes place with formation of carbon monoxide, carbon dioxide, hydrogen, and steam. The luminosity of this zone is due to the presence of the solid carbon particles and dense hydrocarbons, which become incandescent owing to the heat evolved by the chemical reactions which are taking place. (D) Here the products of zones (B) and (C) are mixed with excess of air and burn completely to carbon dioxide and water.

441. The Gas Flame.—A coal gas flame has the same four zones as a candle flame unless the jet is very small. As its size is reduced the luminous zone gradually diminishes relatively to the non-luminous zones, and when the jet is very small it entirely disappears. The flame now consists of three zones only, and presents the appearance shown in Fig. 86.

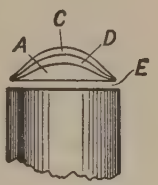


Fig. 86.

A is the zone of no combustion. B is the zone of incomplete combustion; it is blue, like zone B in Fig. 86, to which it corresponds. In the mantle C the combustion is complete. Between the flame and the burner there is a space E containing unburnt gas; it is part of the zone of no combustion.

Exp. 119.—Examine a gas-jet when turned on full, and note the zones as in the candle flame (§ 440). The mantle can be shown to be hot by means of a thin piece of wire held across the flame. Note the changes in the character of the flame as the gas is gradually lowered, and the gradual disappearance of the luminous zone.

442. Luminosity of Flame: (*a*) **History.**—Davy studied the causes of luminosity of flame, and in 1818 advanced the theory that luminosity was due to the incandescence of solid carbon particles. He said that the hydrocarbons were split up into carbon and hydrogen, thus—

$$C_nH_m \rightarrow nC + mH;$$

the hydrogen burns and the carbon becomes incandescent and burns on the edge of the flame. Later, Faraday, in 1852,

siphoned the gases from the parts of a candle flame and found solid carbon only in the upper luminous part. Kersten, in 1861, by his experiments supported Davy's views ; thus he found that the admixture of chlorine with marsh gas increased the luminosity, whereas the admixture of oxygen decreased it, his explanation being as follows :—

$$Cl_2 + CH_4 \quad \text{gave} \quad HCl + C \text{ (solid)},$$

but in the case of $O_2 + CH_4$ the carbon burnt before it could be disseminated through the flame.

Heumann, in 1876, introduced a fresh factor into the problem by showing that an increase in temperature increased the luminosity and *vice versa*, and later he conducted many experiments to indicate that luminosity was due to solid particles in the flame.

Frankland, in 1867, found that there was a direct relation between the luminosity of a flame and the pressure. Thus by comparing the luminosity of the hydrogen flame burning under a pressure of 12 atmospheres with the same flame at 3 atmospheres he found that the luminosity was diminished by 99 per cent. by this reduction in pressure. He stated, therefore, that dense gases and vapours are more luminous than gases of low density, and that feebly luminous flames are rendered more luminous when burning under pressure. His theory was called the " dense hydrocarbon theory," and he stated that luminosity was due to the glow of dense hydrocarbons rather than to the presence of solid particles.

Lewes, in 1896, after collecting and analysing the gases from a Bunsen burner, propounded the theory that acetylene was the " dense hydrocarbon," and was therefore the cause of luminosity. He removed the acetylene before burning and the luminosity was very small, and on the addition of 1·5 per cent. acetylene the luminosity was restored. He said, therefore, that luminosity was due to acetylene formed by decomposition of the other hydrocarbons, and that the acetylene was then decomposed into its elements at the higher temperature of the flame.

Smithell's investigations (about 1895) indicated that there was no free carbon in any of the flames of the hydrocarbons

tried. The carbon was present as carbon monoxide and carbon dioxide, but there was free hydrogen present. Bone's work, extending over a large number of years, led to the conclusion that combustion took place in a number of steps, but that no free carbon or free hydrogen was present at any stage of the process.

Thus an explanation of luminosity to cover all cases cannot yet be given.

443. Luminosity of Flame : (*b*) Summary of Causes.—There are three factors, some or all of which are concerned in the luminosity of flame—

(1) The presence of solid particles ;

(2) The density of the flame gases ;

(3) The temperature.

Davy's solid particle theory stated that (1) and (3) were the sole causes, and it was supported by the following facts :—

(*a*) Most flames in which no solid particles can be present are practically non-luminous : *e.g.* hydrogen burning in oxygen.

(*b*) Non-luminous flames become luminous when solid particles are introduced into them : *e.g.* finely-divided charcoal or lime blown into an oxyhydrogen blowpipe flame makes it luminous.

(*c*) A glass rod held in a candle flame becomes covered with soot only on the under side. If the interior of the flame consisted of vapours which deposited soot because they were cooled down by the rod, the deposit should be all round.

(*d*) Luminous flames, like that of a candle, when placed between a brighter light and a screen, cast a shadow ; non-luminous flames cast no shadow.

That the luminosity of some flames is not due to the presence of incandescent solid particles is shown by the existence of luminous flames in which no solid matter can possibly be formed : *e.g.* the flame produced when phosphorus or phosphoretted hydrogen burns in oxygen, or arsenic burns in nitric

oxide or oxygen. At the temperature of the flame in these cases all the possible products of combustion are gases.

According to *Frankland's theory*, luminosity is due to the presence of heated gases, the luminosity increasing with the density of the gases. This is supported by the following facts :—

(*a*) A candle burns at high altitudes or in an artificially rarefied atmosphere with greatly-reduced luminosity.

(*b*) The flame of hydrogen burning in oxygen becomes luminous when the gases are under a pressure of two atmospheres.

Lewes' theory states that in the case of coal gas and related gases, luminosity is due to the presence of acetylene.

The effect of the temperature of a flame upon its luminosity may be studied by experiment.

Exp. 120.—Make a short coil of stout copper wire by giving it half-a-dozen turns round a piece of glass rod about 5 mm. in diameter, leaving only a small space between one coil and the next. Bring the coil into the upper part of the luminous zone of a candle flame : the flame will become smoky ; if it be quickly depressed to the level of the wick, the flame loses its luminosity, and, indeed, may be extinguished altogether.

Exp. 121.—Fill a gas cylinder with oxygen and lower a lighted candle into it : the flame becomes much shorter and brighter.

In the first case, copper, which is a good conductor of heat, conveys away heat from the flame, and lowers its temperature to such an extent that the solid particles of carbon can no longer keep up their luminosity ; they escape combustion and pass off as smoke. Indeed, the vapours may also be cooled below their ignition point, in which case the flame is extinguished altogether.

In the second case, the heat given out is not utilised in raising the temperature of the nitrogen of the air, but is all available for heating the particles of carbon.

Thus, raising the temperature of a flame increases its luminosity, and lowering its temperature decreases its luminosity.

The effect of cooling is often noticed in very cold weather, when the gas, if carried by exposed pipes, does not possess

its usual illuminating power : this is partly due to the condensation of volatile liquid and solid hydrocarbons contained in the gas, and also to the extra amount of heat required to raise both gas and air to the temperature of incandescence.

In ordinary flames used for various purposes all three causes operate and may be utilised.

444. The Batswing and Fishtail Flames.—In these flames the gas is made to issue from a narrow slit (fishtail) or from two jets which impinge on each other (batswing).

By these devices the flame is flattened. This enlarges the surface of gas exposed to the air, and thus increases the rate of combustion and the luminosity.

445. The Bunsen Flame.—This flame is produced by mixing air with the gas which is to be burned, in such quantity as to render the combustion nearly perfect and the flame non-luminous. The gas is supplied through a small jet placed inside a wide tube, so that the rush of gas sucks in air through holes at the bottom ; the mixture of gas and air passes up the tube, and is ignited at its mouth.

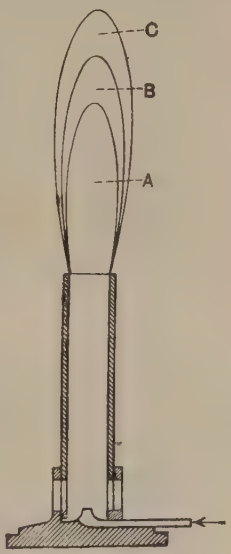


Fig. 87.

The Bunsen flame consists of three zones (Fig. 87). A is the zone of no combustion. In B (pale blue) incomplete combustion takes place, the hydrocarbons being in excess, and in C (very pale blue) the combustion is complete, air being in excess.

The non-luminosity of a Bunsen flame is caused by (1) increased oxidation by which the separation of solid particles of carbon is prevented, or at any rate reduced ; (2) dilution by the nitrogen of the air—this raises the temperature required for the decomposition of the hydrocarbons of coal gas ; (3) cooling by the large volume of air introduced. The result of

(2) and (3) is that the gases reach the outer zone where air is in excess and are completely burnt up before they attain the temperature at which dense hydrocarbons are formed and carbon particles separate.

446. Oxidising and Reducing Flames.—The foregoing paragraphs show that heated hydrocarbon vapours have the power of combining with oxygen in the gaseous condition to form carbon monoxide or dioxide, hydrogen, and water vapour. They have thus the power of abstracting oxygen from many solid oxides or bodies containing oxygen. This property may readily be shown either by means of the flame of a Bunsen burner or of the blowpipe.

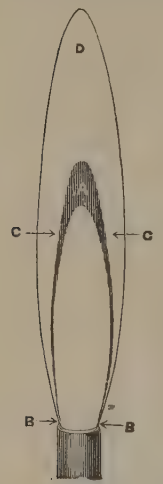


Fig. 88.

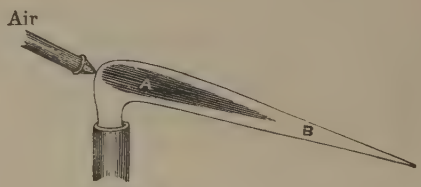


Fig. 89.

In Fig. 88
A is reducing area
BCD is oxidising area
B low temperature oxidising area
C high „ „ „

In Fig. 89
A is reducing area
B is oxidising area

Exp. 122.—Partially close the holes at the base of the Bunsen burner until there appears a well-defined luminous tip (A in Fig. 88) within the flame owing to the reduction of the air supply. Now introduce within the luminous area a small amount of barium sulphate on a loop of thin platinum wire, and hold it there steadily for two or three minutes. The barium sulphate is reduced to barium sulphide which on treatment

with dilute hydrochloric acid is transformed into the soluble chloride of barium with the evolution of sulphuretted hydrogen (H_2S)—

$$BaS + 2\,HCl = BaCl_2 + H_2S.$$

Similarly, oxide of lead or copper may be reduced to metallic lead or copper when brought into the inner flame A of the blowpipe (Fig. 89). Wherever in a flame the hydrocarbons predominate and the supply of oxygen is limited such a *reducing* action prevails; and wherever in a flame the supply of oxygen is in excess of that required to consume the hydrocarbons, as in the outer zone of the candle or the Bunsen burner or the blowpipe flame, an *oxidising* action is experienced. This may be shown by bringing metallic tin or other metals into the outer margin of the Bunsen flame.

447. Temperature of Flames.—In the following table the maximum temperature of various flames is given—

Bunsen burner	1,870° C.
Air blowpipe	2,200° C.
Oxy-hydrogen blowpipe	2,400° C.
Oxy-acetylene	2,600° C.

In connection with these the two following estimated temperatures may be given :—Electric arc, 3,300° C.; Sun, 8,000° C.

448. Definition of "Combustion."—The term *combustion* has hitherto been used in the popular sense to indicate the burning of a substance in air. Chemists, however, usually assign a broader meaning to the term, as follows :—*Combustion is chemical reaction between two substances accompanied by the production of heat and light.* There is no restriction as to the nature of the reacting substances. Some writers include under the term combustion such processes of oxidation as the rusting of iron in moist air, in which heat only, not light, is produced; but this is, perhaps, carrying the use of the term too far.

Usually the substance which is *outside* during the combustion is spoken of as a *supporter of combustion*, and that which is

inside as the *combustible body*; but, as has been shown above in the case of coal gas and air, the supporter of combustion and the combustible body can change places. This holds also in other cases, so that the terms are only relative.

Since the external substance is usually air, a substance is commonly said to be combustible or not according to whether it will or will not burn in air. Thus, hydrogen, phosphorus, and carbon monoxide are combustible; chlorine and nitrous oxide are not combustible.

Again, a substance is said to be a *supporter of combustion* if it will allow the same substances to burn in it as burn in air (*e.g.* coal gas, hydrogen, a taper). Chlorine and nitrous oxide are supporters of combustion; sulphuretted hydrogen, carbon monoxide, and hydrogen are not.

Strictly speaking, however, any two substances which can exist in the gaseous state and which can combine chemically with sufficient evolution of heat may occupy towards each other the positions of supporter of combustion and combustible body interchangeably. For example, a jet of hydrogen will burn in chlorine, and a jet of chlorine will burn in hydrogen. In the former case hydrogen is the combustible body and chlorine the supporter of combustion; in the latter the reverse. Again, phosphorus burns in oxygen; but it would be possible to burn oxygen in phosphorus vapour, in which case the latter would be the supporter of combustion.

449. Heat of Combustion.—Whenever carbon, hydrogen, or bodies containing carbon and hydrogen burn, by combining with the oxygen of the air (the carbon to form carbon monoxide or dioxide, and the hydrogen to form water), the amount of heat accompanying the change is perfectly definite and constant.

If a gramme of pure carbon be burnt to carbon dioxide, the heat given out will be sufficient to raise the temperature of 8,080 c.cm. of water 1° C.; this is expressed shortly by the statement that the *heat of combustion* of one gramme of carbon is 8,080 thermal units or calories. So, in like manner, the combustion of one gramme of hydrogen is found to give rise to the evolution of 34,200 thermal units. Hydrogen, there-

fore, on combustion gives out more than four times the amount of heat evolved by the same weight of carbon.

Bituminous coal consists chiefly of carbon, but, as it contains some hydrogen, it should give out more heat on combustion than the same weight of carbon, and it would do so but for the fact that it contains usually 15 to 20 per cent. of oxygen, sulphur, nitrogen, and mineral ash, which are practically unproductive of heat. In anthracite, however, these constituents amount to little more than 5 per cent., and the heat of combustion of this kind of coal is greater than that of bituminous coal.

Petroleum, consisting entirely of carbon and hydrogen, and containing much more hydrogen than coal, actually does give out more heat than the same weight of carbon.

Fuel being employed for heating purposes, the amount of heat generated in its combustion is of primary importance, and the following table shows at a glance the comparative value of different substances which are applicable as fuels :—

Hydrogen ...	34,200	thermal units per gramme consumed.
Petroleum ...	12,000	,, ,,
Coal	7,500 to 8,500	,, ,,
Carbon ...	8,080	,, ,,
Wood	about 3,000	,, ,,

QUESTIONS.—CHAPTER XXIII.

1. Explain the term *incandescence*, and describe experiments which show how it may be produced.

2. What conditions are necessary for the production and continuance of combustion ? How would you show them experimentally ?

3. Describe an experiment by which air may be made to burn in coal gas.

4. Explain what is meant by *point of ignition* and *flash point*.

5. Explain the principle of the *Davy lamp*, and describe an experiment which illustrates it.

6. Describe the structure of a candle flame, and explain the nature of the chemical changes which take place in the different zones.

7. Describe the appearance of a coal-gas flame which is burning very low.

8. Discuss the explanations which have been put forward to account for the luminosity of flame.

9. Give a diagram of the Bunsen flame, and indicate on it—

(*a*) the reducing area ;

(*b*) the oxidising area ;

(*c*) the high temperature oxidising area ;

(*d*) the low temperature oxidising area.

10. What are the causes of the non-luminosity of a Bunsen flame ?

11. How may calcium sulphate be reduced to calcium sulphide—

(*a*) in the blowpipe flame ;

(*b*) in the Bunsen flame ?

12. Explain carefully what you understand by *combustion*, and *supporter of combustion*.

13. What volume of water may be raised from 10° C. to 50° C. by the heat derived from the combustion of 10 grm. of hydrogen and 10 grm. of carbon respectively ?

14. Explain the term *heat of combustion*, and compare the heats of combustion of the common kinds of fuel.

CHAPTER XXIV.

OXIDES OF CARBON. CARBON DISULPHIDE. CARBONYL CHLORIDE.

The chief oxides of carbon are carbon monoxide, CO, carbon dioxide, CO_2, and carbon suboxide, C_3O_2.

Carbon Monoxide, CO.

450. History.—Carbon monoxide was first prepared in 1776 by F. de Lassone by reducing lead monoxide with carbon—

$$PbO + C = Pb + CO.$$

Later, Priestley, in 1796, used iron oxide and charcoal, but did not understand the constitution of the gaseous product. Lavoisier knew that carbon monoxide on combustion gave carbon dioxide, but it was left to M. Cruickshank in 1800, and Clément and Désormes in 1801, to show the true composition of the gas.

451. Occurrence.—This gas occurs in small quantity in chimney gases, especially where the air-supply during combustion is not in sufficiently large excess; it is also formed during the dry distillation of wood, coal, and such organic bodies. The gases from blast or other furnaces in which an excess of carbon is present, and in which a reducing operation is being performed, consist largely of carbon monoxide.

452. Preparation.—(1) Carbon monoxide may be prepared conveniently in the laboratory by gently warming a mixture of sodium formate and concentrated sulphuric acid—

$$H.COONa + H_2SO_4 = NaHSO_4 + H_2O + CO.$$

Formic acid may also be used—

$$HCOOH + H_2SO_4 = H_2SO_4.H_2O + CO.$$

(2) By heating oxalic acid with concentrated sulphuric acid, when equal volumes of carbon dioxide and carbon monoxide are obtained at the same time—

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + H_2SO_4 = CO + CO_2 + H_2SO_4.H_2O.$$

The evolved gases can be passed through a wash-bottle containing a solution of caustic soda to absorb the carbon dioxide.

(3) By heating roughly-powdered potassium ferrocyanide, $K_4FeC_6N_6 + 3\ H_2O$, with concentrated* sulphuric acid. The change which takes place is represented by the equation—

$$K_4FeC_6N_6 + 6\ H_2SO_4 + 6\ H_2O = 2\ K_2SO_4 + FeSO_4 + 3\ (NH_4)_2SO_4 + 6\ CO.$$

The water required for this reaction is derived partly from the water of crystallisation of the ferrocyanide and partly from the 1·5 per cent. of water present in the sulphuric acid.

(4) By reduction of carbon dioxide—

An interesting method whereby carbon monoxide may be obtained in large quantities, though in an impure condition, is to pass carbon dioxide over red-hot charcoal. The charcoal may conveniently be heated in an iron pipe by means of a combustion furnace, and the carbon dioxide evolved in a gentle stream by the action of hydrochloric acid on marble—

$$CO_2 + C = 2\ CO.$$

The carbon monoxide is either collected or burnt at a jet attached to the exit of the tube.

This method of formation may be observed in a coke or red-hot cinder fire, on the surface of which the blue flames of the burning gas may be seen. The air passing in at the base of the fire at the lower part of the grate unites with carbon,

* *Dilute* sulphuric acid gives rise to the formation of hydrocyanic acid (HCN).

forming carbon dioxide, and this as it passes over the mass of red-hot carbon in the upper part of the grate is transformed into carbon monoxide. "Producer gas" (see §§ 432, 433) or "generator gas," used in some manufacturing operations, and "water gas" (see § 434) consist largely of carbon monoxide.

(5) Carbon monoxide is formed by heating certain metallic oxides with carbon—

$$C + ZnO = CO + Zn,$$

and this explains the reducing action of carbon in the preparation of metals. The reduction of a carbonate by carbon or a metal often yields carbon monoxide—

$$BaCO_3 + C = 2\,CO + BaO$$
$$4\,CaCO_3 + 3\,Fe = 4\,CO + 4\,CaO + Fe_3O_4.$$

453. Properties.—Carbon monoxide is a colourless, tasteless gas; it is only very slightly soluble in water, 100 volumes of water at ordinary temperatures dissolving less than three volumes of the gas. It is also very difficult to condense, the liquid boiling under atmospheric pressure at $-190°$ C. and freezing to white crystals at $-200°$ C. Under ordinary circumstances, carbon monoxide burns in air with a fine bluish flame, or may be exploded with oxygen in a eudiometer, forming carbon dioxide. But when the gases are *perfectly dried* by exposing them for a lengthened period to phosphorus pentoxide, sparks may be passed through the mixture without combination taking place. This affords us with yet another example of the influence of moisture in assisting chemical reaction.

Owing to the readiness with which carbon monoxide combines with oxygen, it is a powerful reducing agent at high temperatures. It is an unsaturated compound, the carbon atom in its molecule being divalent, whereas the normal valency of carbon is four. It thus forms addition compounds, *e.g.* it combines directly with the vapour of sulphur, forming carbonyl sulphide (COS), and in sunlight with chlorine, forming carbonyl chloride ($COCl_2$), also known as phosgene gas.

Finely-divided nickel and iron unite with carbon monoxide

on heating, forming compounds called *carbonyls*; nickel carbonyl is represented by the formula $Ni(CO)_4$ and iron carbonyl by $Fe(CO)_5$; both these compounds are liquids.

Carbon monoxide dissolves in a solution of cuprous chloride in strong hydrochloric acid or ammonia, with formation of a compound $Cu_2Cl_2 \cdot CO$. A solution of cuprous chloride is used as an absorbent for CO in gas analysis. If the gas is passed over solid caustic soda at a temperature of 200° C., sodium formate is formed—

$$NaOH + CO = HCOONa.$$

Carbon monoxide is a very poisonous gas, this property depending on its power of combining with the haemoglobin of the blood to form a bright red compound, carboxyhaemoglobin. The haemoglobin is then unable to perform its function of distributing oxygen to the various parts of the body.

454. Composition.—The composition of carbon monoxide may be ascertained by exploding the gas in a eudiometer along with oxygen. It will be found that 100 volumes of carbon monoxide and 100 volumes of oxygen after explosion show a contraction of 150 volumes, and on absorbing the carbon dioxide formed by means of potash, 50 volumes of oxygen will remain. Thus 100 volumes of carbon monoxide have united with 50 volumes of oxygen to form 100 volumes of carbon dioxide.

This agrees with the formula CO for carbon monoxide assuming the formula for carbon dioxide to be CO_2 (see § 462 for proof of this)—

$$\underset{\text{4 vols.}}{2\,CO} + \underset{\text{2 vols.}}{O_2} = \underset{\text{4 vols.}}{2\,CO_2}.$$

The density of carbon monoxide affords a confirmation of this formula. The gas is fourteen times as heavy as hydrogen, and therefore its molecular weight is $2 \times 14 = 28$, that of hydrogen being 2.

Now $C = 12$, $O = 16$, and therefore $CO = 12 + 16 = 28$, so that, as already stated, CO is the correct formula for carbon monoxide.

455. Detection and Estimation of Carbon Monoxide.—Carbon monoxide may be detected by—

(1) Burning with a blue flame to give carbon dioxide only.

(2) Shaking with diluted blood, when carboxyhaemoglobin is obtained.

(3) A delicate test for carbon monoxide is based on the reduction of iodine pentoxide to iodine by the gas—

$$I_2O_5 + 5\ CO = I_2 + 5\ CO_2.$$

It can be estimated by absorption in ammoniacal cuprous chloride, after removing carbon dioxide, etc.

Carbon Dioxide (Carbonic Acid Gas), CO_2.

456. History.—The Dutch chemist, Van Helmont, early in the seventeenth century, was the first to recognise carbon dioxide as a distinct substance, which he called *gas sylvestre* (wild gas of the woods). He showed that it is evolved by the fermentation of wine and beer, and by the burning of charcoal; and that it extinguishes a lighted candle.

The most important pioneer work on carbon dioxide, however, was done about 1755 by Joseph Black. He called the gas *fixed air*, because he first showed that it is contained in limestone and in *Magnesia alba*,* and is evolved from these substances by heat or by the action of a dilute acid. Black's work put an end to the old idea that the carbonates were elements, and gave the first rational explanation of the conversion of the "mild" alkalies (Na_2CO_3, K_2CO_3) into "caustic" alkalies (NaOH, KOH) by the action of lime.

Lavoisier synthesised carbon dioxide from carbon and oxygen in 1781, and called it *acide carbonique*, although it is really the anhydride of carbonic acid.

457. Occurrence.—This gas is of more frequent occurrence than carbon monoxide. Its presence in air and water has already been mentioned, and also the part it plays in the animal and vegetable kingdoms. It is given off in large

* A mixture of hydroxide and carbonate of magnesium.

quantities from lime-kilns, in which the limestone ($CaCO_3$) is decomposed by heat into quicklime (CaO) and carbon dioxide.

Processes of fermentation and putrefaction give rise to the gas. Whenever an explosion of fire-damp occurs in coal mines carbon dioxide is formed in large quantities, and constitutes what the miners call the *after-damp* or *choke-damp*. Carbon dioxide is found in solution in many natural waters.

458. Preparation.—The usual method of preparing carbon dioxide is by the action of dilute hydrochloric acid on limestone or marble, using the apparatus shown in Fig. 90. A Woulfe's bottle containing a little water dissolves any hydrochloric acid carried over by the carbon dioxide, which is collected by displacement of air. The reaction which takes place is represented by the equation—

$$CaCO_3 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

Although somewhat soluble in water, the gas may be collected over water, but as it is much heavier than air it is usually collected by downward displacement. All carbonates, when treated with dilute hydrochloric acid, liberate carbon dioxide; many, such as limestone, liberate it when heated.

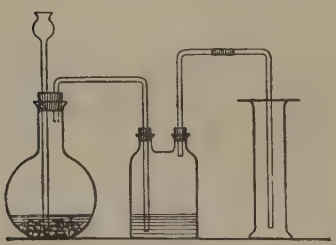


Fig. 90.

Carbon dioxide is formed when carbon or compounds containing it are burnt in excess of air. If carbon compounds are heated to redness with oxide of copper, the whole of the carbon is transformed into carbon dioxide, and it is in this way that the amount of carbon in such compounds is estimated.

459. Properties of Carbon Dioxide.—Carbon dioxide is a colourless gas with a faintly acid taste and smell. It is about $1\frac{1}{2}$ times as heavy as air, and its high density may be illustrated by the following experiment :—

Exp. 123.—Fill a large beaker of three or four litres capacity by downward displacement with carbon dioxide; now detach a soap-bubble charged with air into the beaker, and it will be found to float on the surface of the heavier carbon dioxide.

Carbon dioxide is soluble in water, which at 15° C. dissolves about its own volume of the gas, while at 0° C. 100 volumes of water dissolve 180 volumes of the gas. As with other gases, the amount dissolved increases directly as the pressure under which solution takes place, and soda-water being water charged with the gas under about four atmospheres pressure contains about four times its volume of the gas.

The aqueous solution of carbon dioxide possesses feebly acid properties, for it is able to change the colour of litmus from blue to *claret* (not to the *bright red* produced by strong acids such as HCl and H_2SO_4); carbon dioxide can also, like other acids, decolourise phenolphthalëin which has been rendered pink by the addition of a small quantity of alkali.

Exp. 124.—Pass a stream of carbon dioxide through a few cubic centimetres of water to which some drops of litmus solution have been added, and note that the litmus assumes a claret tinge; contrast this with the effect of adding litmus to water containing a little hydrochloric or sulphuric acid. Notice also that by boiling, the carbon dioxide is expelled, and the litmus assumes its original colour. A solution of carbon dioxide in water is therefore very unstable, and possessed of a feebly acid character.

Exp. 125. Pass the expired air from the lungs, or carbon dioxide prepared from marble and washed free from hydrochloric acid by passing through water, through a slightly alkaline pink solution of phenolphthalëin; the pink liquid becomes colourless.

Carbon dioxide is in general a non-supporter of combustion and of animal life. Certain metals, however, such as magnesium and potassium, will burn in it with liberation of carbon—

$$2\,Mg + CO_2 = 2\,MgO + C$$

$$4\,K + 3\,CO_2 = 2\,K_2CO_3 + C.$$

When carbon dioxide is strongly heated it dissociates into carbon monoxide and oxygen—

$$2\,CO_2 \rightleftharpoons 2\,CO + O_2.$$

Carbon dioxide is decomposed by the green colouring-matter of plants in presence of sunlight, carbon being assimilated and oxygen set free in the process.

Though the harmful effects of carbon dioxide are mainly due to suffocation (*i.e.* absence of oxygen), yet at the same time the gas does exercise a directly poisonous action on the system; for air containing more than one volume of it per thousand (*i.e.* about three times the normal quantity) has a distinctly depressing effect, and often gives rise to headache.

460. Liquid and Solid Carbon Dioxide.—Under a pressure of 34 atmospheres at 0° C. the gas condenses to the liquid form, and in this form it is prepared on a large scale and stored in steel cylinders. If the nozzle of one of these cylinders is opened, the pressure being released, the liquid is rapidly transformed into gas. The amount of heat absorbed by the passage from the liquid to the gaseous condition is considerable, and the issuing gas becomes so far cooled that a part of it condenses again even to the solid form. Solid carbon dioxide is a white, snow-like substance which passes only comparatively slowly into the gaseous condition again. The depression of temperature caused by its passage from the solid to the gaseous condition is such that mercury can be readily cooled down to — 40° C. and obtained as a solid body.

461. Uses of Carbon Dioxide.—Carbon dioxide is used in sugar refineries, white lead factories, and in the manufacture of bicarbonates, particularly in the Solvay Process. Liquid carbon dioxide is used very extensively for effervescing drinks, in breweries, in metallurgy, for refrigerating machinery, and for making borings, etc.

462. Composition of Carbon Dioxide.—This may be shown by a method similar to that employed in the case of sulphur dioxide. Thus when carbon is burnt in oxygen no change of volume occurs, and carbon dioxide is therefore said to contain its own volume of oxygen. It follows from Avogadro's hypothesis that the formula for the gas may be written C_xO_2 where x has yet to be determined. Now the molecular weight

of carbon dioxide as deduced from its density is 44. This agrees with the value $x = 1$ in the formula just given for C = 12, O = 16, and $C_1O_2 = 12 + 2 \times 16 = 44$. The formula for carbon dioxide is therefore CO_2.

The composition by weight of the gas agrees with this formula, for, as already stated in §§ 393, 406, 12 parts by weight of carbon unite with 32 parts of oxygen to produce 44 parts of carbon dioxide.

463. Detection and Estimation of Carbon Dioxide.—Carbon dioxide can readily be detected by its property of precipitating calcium carbonate from lime water.

It can be estimated by absorption in a strong solution of caustic potash. In solution (as carbonates or bicarbonates), it can be estimated by titration against an acid.

464. The Carbonates.—We have seen in a previous paragraph that a solution of carbon dioxide in water shows a feebly acid reaction. Carbonic acid turns litmus a "claret" colour and decolorises pink phenolphthalëin. For this reason, and from a consideration of the salts known as the carbonates, carbon dioxide is to be regarded as the anhydride of carbonic acid, and the composition of the acid, although never isolated, may be taken as H_2CO_3—

$$O=C=O + H-O-H \rightarrow \begin{matrix} HO \\ HO \end{matrix}\!\!>\!C=O$$

Carbonic acid has two atoms of hydrogen replaceable by metals, and is therefore a *dibasic* acid. In the acid carbonates or *bicarbonates* only half the hydrogen is so replaced; thus $KHCO_3$ is bicarbonate of potash, and $NaHCO_3$ is bicarbonate of soda. In the normal carbonates the whole of the hydrogen is replaced, as with K_2CO_3, potassium carbonate, and Na_2CO_3, sodium carbonate.

Exp. 126.—Pass carbon dioxide to saturation into a solution of caustic soda, and then evaporate down to dryness on a water-bath. A

residue will be obtained consisting of the monohydrated normal carbonate of soda, $Na_2CO_3 \cdot H_2O$.

Dissolve as much as possible of this in hot water and allow to cool; crystals of $Na_2CO_3 \cdot 10\ H_2O$ will be formed. This is the product known as "soda crystals," and used as washing soda.

On very gently warming a quantity of soda crystals, or preferably $Na_2CO_3 \cdot H_2O$, in an atmosphere of carbon dioxide, it takes up CO_2 and is transformed into the bicarbonate, $NaHCO_3$—

$$Na_2CO_3 \cdot H_2O + CO_2 = 2\ NaHCO_3.$$

Exp. 127.—Heat in a porcelain basin over the Bunsen flame a few grammes of dry bicarbonate of soda; carbon dioxide will be given off, and the normal carbonate reproduced—

$$2\ NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbonates and bicarbonates of the alkali metals are obtained by means of such reactions; they are soluble in water. The carbonates of other metals are insoluble in water, but the bicarbonates are soluble. Thus $CaCO_3$ is insoluble, but $Ca(HCO_3)_2$ is soluble.

The insoluble carbonates may be obtained—

(1) by the addition of sodium or potassium carbonate to a soluble salt of the metal—

$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2\ NaCl;$$

(2) By passing carbon dioxide into a solution of the hydroxide—

$$Ca(OH)_2 + CO_2 = CaCO_3* + H_2O.$$

Weak bases such as alumina, oxide of silver, and oxide of mercury either form no carbonates or very unstable ones, and the normal carbonates of the alkali metals are the only ones which withstand a high temperature without decomposition. All other carbonates when heated give off carbon dioxide and form an oxide of the metal (except ammonium carbonate which decomposes into ammonia, carbon dioxide, and water).

* Excess of CO_2 transforms this into the soluble bicarbonate—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

465. Test for Carbonates.—Add dilute hydrochloric acid to the solid carbonate, or an aqueous solution of a carbonate in a test-tube. An effervescence will be observed, and on decanting the gas downwards into a second tube containing lime-water, and shaking up, a turbidity will be produced in the lime-water owing to the formation of calcium carbonate.

466. Distinction between Normal Carbonates and Bicarbonates.—The test just given applies to both normal carbonates and bicarbonates. If, however, the carbonate is insoluble in water, it must be a normal salt. If it is soluble the following tests will decide to which class it belongs :—

(1) Add magnesium sulphate to the solution. Normal carbonates give an immediate white precipitate ; bicarbonates only give a precipitate on boiling—

$$Na_2CO_3 + MgSO_4 = MgCO_3 + Na_2SO_4$$

$$2\,NaHCO_3 + MgSO_4 = \underset{\text{(soluble)}}{Mg(HCO_3)_2} + Na_2SO_4$$

on boiling

$$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO_2.$$

(2) Boil the solution. Bicarbonates evolve carbon dioxide with effervescence ; normal carbonates do not undergo decomposition.

Carbon Disulphide, CS_2.

467. Occurrence and Properties.—This compound occurs in traces in coal gas, and is formed in quantity when sulphur vapour is passed over red-hot charcoal. It is prepared commercially by heating sulphur and coke together in an electric furnace—

$$C + 2\,S = CS_2.$$

It is a colourless liquid of density 1·3 at 0° C., boiling at 46° C. and freezing at — 110° C. ; it refracts light strongly, is very volatile, and gives off a very inflammable vapour. When pure it has a sweetish, ethereal smell, but usually the impurities which it contains render it very disagreeable.

One of its most remarkable properties is its solvent action; indiarubber, fats, and some of the non-metallic elements such as phosphorus, sulphur, and iodine, which are otherwise difficult to obtain in solution, are readily dissolved by carbon disulphide.

In consequence of its high refractive power for light, it is frequently employed as a means of producing a spectrum, the liquid being introduced into a hollow glass prism.

CS_2 is the analogue in composition of CO_2, and thiocarbonic acid (H_2CS_3), the analogue of carbonic acid (H_2CO_3) is known; CS corresponding to CO and COS have also been obtained. Thus a number of bodies are known containing sulphur in place of oxygen, the sulphur compound resembling the corresponding oxygen compound in chemical properties.

468. Carbonyl Chloride.—Carbonyl chloride, $COCl_2$, or *phosgene*, may be prepared by passing a mixture of equal volumes of chlorine and carbon monoxide over gently heated animal charcoal—

$$CO + Cl_2 = COCl_2.$$

It is also prepared by the action of carbon tetrachloride on fuming sulphuric acid—

$$2\,SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2.$$

Carbonyl chloride is a colourless gas, which liquefies at 8° C. and freezes at −127° C. It is very poisonous and reacts with water to give carbon dioxide and hydrochloric acid—

$$COCl_2 + H_2O = CO_2 + 2\,HCl.$$

QUESTIONS.—CHAPTER XXIV.

1. Mention some conditions under which carbon monoxide is produced during the combustion of fuel on the large scale.

2. You desire to collect a specimen of CO as free as possible from air or CO_2, using oxalic acid as the source of the gas; how would you proceed?

3. Describe the preparation of carbon monoxide from sodium formate and sulphuric acid.

4. What is the action of dilute and of concentrated sulphuric acid on potassium ferrocyanide?

5. How may CO be transformed into CO_2 and CO_2 into CO ?

6. Write a short account of the properties of carbon monoxide.

7. It has been shown that chemical action undergoes modification when the reacting substances are perfectly dried ; give instances of this.

8. How would you prove that carbon monoxide has the composition indicated by the formula CO ?

9. What experiments would you perform in order to distinguish between—

(*a*) CO and CO_2 ;

(*b*) CO_2 and a mixture of CO and CO_2 containing large excess of CO_2 ;

(*c*) CO and a mixture of CO and CO_2 containing large excess of CO ?

10. Write a short history of carbon dioxide.

11. Describe the reactions which take place when sodium bicarbonate ($NaHCO_3$) and lead carbonate ($PbCO_3$) are respectively subjected to the action of heat, and when they are brought into contact with dilute nitric acid.

12. Write down in separate columns (*a*) the physical, (*b*) the chemical properties of carbon dioxide.

13. Give two methods for the decomposition of carbon dioxide.

14. How may it be demonstrated that carbon dioxide has the formula CO_2 ?

15. Discuss the constitution of carbonic acid.

16. How are carbonates in general formed ? Given metallic zinc, lime, and caustic potash, how would you prepare specimens of zinc, carbonate, calcium carbonate, and potassium carbonate ?

17. By what tests can *normal* carbonates be distinguished from *acid* carbonates ?

18. What are the *characteristic* properties of carbon disulphide ? What are the products formed, and their relative volumes, when this body is burnt in oxygen ?

19. How is carbonyl chloride prepared ? What are its properties ?

20. 15 c.cm. of carbon monoxide were exploded with 20 c.cm. of oxygen. After treating the product with excess of caustic potash 12·5 c.cm. of gas remain. Deduce from this the formula for carbon monoxide assuming carbon dioxide to be represented by CO_2.

CHAPTER XXV.

SILICON AND BORON.

469. Introductory.—These two elements, together with carbon, closely resemble each other in many of their properties. Thus all of them exhibit allotropic modifications, one at least of which is crystalline and possesses a pronounced lustre; also, they are all very infusible. Each of them combines directly with oxygen to form an oxide possessing feebly acidic properties, but the union only takes place at high temperatures, especially in the case of the crystalline modifications.

Silicon, Si.

470. History.—Becher (1655) regarded silica (silica from *silex*, a flint), SiO_2, as an "earth," and called it *terra vitrescibilis*, because it was used in glass making. Later in 1660, Tachenius proved that silica dissolved in fused caustic alkalies, and must therefore possess acidic properties.

It was not till the time of Lavoisier that silica, long known in the more or less pure forms of quartz, sand, flint, opal, etc., was suspected, from its way of combining with metallic oxides, to be itself a compound; Lavoisier himself regarded it as an oxide of an unknown element. Scheele, who worked on silicon fluoride, SiF_4, and the silicic acids, said silica had the nature of a refractory acid. It was, however, Gay-Lussac and Thénard who first prepared elementary silicon by passing gaseous silicon fluoride over heated potassium.

Berzelius, in 1823, obtained the element from potassium silicofluoride by the method described below.

471. Occurrence.—Silicon, always occurring in combination with oxygen as silica (SiO_2), is widely distributed, and forms the predominant constituent of many minerals and rocks. Quartz, sand, agate, and kieselguhr (a finely-divided siliceous material of organic origin) are essentially pure silica, whilst sandstone must be regarded as silica associated with varying quantities of oxide of iron, or alumina. Shale or clay consists of silica and alumina in more or less definite proportions, and a large body of mineral silicates of common occurrence, such as felspar, serpentine, steatite, are very rich in silica. The element silicon is not found in the free state, and is not easy to isolate from its compounds, so that although it constitutes nearly one-fourth of the mass of the earth's crust it is yet a substance rarely met with even in the laboratory.

472. Preparation.—*Amorphous silicon* is obtained by the action of sodium, potassium, or aluminium on silicon tetrachloride ($SiCl_4$), or on potassium silicofluoride (K_2SiF_6), in an atmosphere of hydrogen, or under such other conditions as to exclude oxidation—

$$SiCl_4 + 4\,K = 4\,KCl + Si$$

$$K_2SiF_6 + 4\,K = 6\,KF + Si.$$

The residue is washed free from the potassium salts, which are readily soluble in water, and the silicon remains usually as a brown, amorphous powder.

Amorphous silicon is also obtained by heating sand and magnesium powder together in a glass tube when the magnesium combines with the oxygen of the silica and sets free silicon—

$$SiO_2 + 2\,Mg = Si + 2\,MgO.$$

After cooling, the magnesium oxide is dissolved out from the mass by dilute hydrochloric acid, leaving a residue of silicon.

Crystalline silicon may be prepared by heating sodium silicofluoride (Na_2SiF_6) with excess of aluminium. The silicon set free dissolves in the molten aluminium, and, on cooling, separates out in needle-shaped crystals. To remove the

aluminium, the mass is treated with hydrochloric acid. Essentially this method, and most methods, consist in crystallising silicon from a metal. Crystalline silicon is made commercially by heating quartz with coke in the electric furnace.

473. Properties.—*Amorphous silicon* is a brown powder of density 2·35 which can only be fused and volatilised at the temperature of the electric furnace. It burns readily in oxygen and on strongly heating in air with formation of silica (SiO_2). The only acid in which it dissolves is hydrofluoric acid; hydrogen is evolved and fluosilicic acid (H_2SiF_6) is formed—

$$Si + 6\,HF = H_2SiF_6 + 2\,H_2.$$

Silicon is also dissolved by hot caustic potash solution with formation of potassium silicate and evolution of hydrogen—

$$Si + 2\,KOH + H_2O = K_2SiO_3 + 2\,H_2.$$

Silicon combines directly with fluorine at the ordinary temperature with incandescence, forming silicon tetrafluoride (SiF_4); it also combines with chlorine on heating, yielding silicon tetrachloride ($SiCl_4$). Silicon combines with nitrogen forming silicon nitride and also with certain metals forming silicides.

Crystalline silicon is a very hard substance crystallising in dark-red rhombic octrahedra; its specific gravity is considerably higher than that of amorphous silicon. It does not burn in air even at very high temperature, but behaves towards fluorine and chlorine just as amorphous silicon does. It is insoluble in any single acid, but dissolves in a mixture of hydrofluoric and nitric acids. Crystalline silicon is not so reactive as the amorphous variety, and has certain metallic properties.

Silicon Hydride, SiH_4.

474. Preparation.—On treating magnesium silicide with dilute hydrochloric acid, it yields the hydride, SiH_4, a gaseous body analogous to marsh gas, CH_4.

$$Mg_2Si + 4\,HCl = 2\,MgCl_2 + SiH_4.$$

Mg_2Si is produced by heating sand with excess of magnesium filings—

$$4\,Mg + SiO_2 = Mg_2Si + 2\,MgO.$$

The same compound may be obtained by heating together metallic sodium and potassium silicofluoride (after the manner requisite to obtain silicon) in the presence of *anhydrous* magnesium chloride—

$$8\,Na + K_2SiF_6 + 2\,MgCl_2 = Mg_2Si + 2\,KF + 4\,NaF + 4\,NaCl$$

As thus obtained silicon hydride is mixed with other silicon hydrides and with free hydrogen, produced by the action of hydrochloric acid on the free magnesium present in the magnesium silicide.

The pure gas is prepared by the action of sodium on triethyl silicoformate, $SiH(OC_2H_5)_3$, the sodium acting as a catalytic agent—

$$4\,SiH(OC_2H_5)_3 = SiH_4 + 3\,\underset{\text{Ethyl silicate.}}{Si(OC_2H_5)_4}.$$

475. Properties.—Silicon hydride is a colourless, somewhat unstable gas, decomposing at a red-heat into amorphous silicon and hydrogen. It can be condensed to a liquid boiling at — 112° C. and solidifying at — 185° C. Silicon hydride burns in air with formation of silica and water—

$$SiH_4 + 2\,O_2 = SiO_2 + 2\,H_2O,$$

and when mixed with hydrogen, as in the preparation from magnesium silicide described above, is spontaneously inflammable. It takes fire spontaneously in chlorine, whether pure or mixed with hydrogen, silicon tetrachloride and hydrochloric acid being produced (cf. Methane, § 410)—

$$SiH_4 + 4\,Cl_2 = SiCl_4 + 4\,HCl.$$

Other silicon hydrides known are silicoethane, Si_2H_6, silicopropane, Si_3H_8, silicobutane, Si_4H_{10}, etc.

Silicon Fluoride, SiF_4.

476. Preparation.—This compound is obtained by the direct union of silicon and fluorine at the ordinary temperature, or by the action of hydrofluoric acid on silica or a silicate—

$$SiO_2 + 4\,HF = SiF_4 + 2\,H_2O.$$

Exp. 128. Make an intimate mixture of about 10 grm. of silica or fine white sand with twice its weight of calcium fluoride or finely-powdered fluorspar, and introduce it into a *dry* 8-oz. flask, with enough *concentrated* sulphuric acid to form a thin paste. Fit a cork and delivery tube (Fig. 91), bent twice at right angles, into the flask; on gently heating, silicon fluoride will be given off. If the gas is passed into water (50 c.cm.), gelatinous silica separates out and a solution of fluosilicic acid is formed—

$$3\,SiF_4 + 4\,H_2O = H_4SiO_4 + 2\,H_2SiF_6.$$

In order to prevent the delivery tube becoming stopped up by the gelatinous silica, a little mercury is poured into the cylinder and the delivery tube arranged so that it just dips below the surface of this. Pour off some of the clear liquid after the gas has been passed for some minutes, and show its acid reaction by means of litmus paper. Add potassium carbonate; carbon dioxide is given off with effervescence, whilst a fine white powder will separate out, consisting of potassium silicofluoride, K_2SiF_6, one of the most insoluble of the salts of potassium. The gelatinous silica may be washed by decantation. To do this, pour off the clear liquid as completely as possible, then fill the cylinder with water, and after allowing time to settle, decant off the clear liquid, repeating the operation several times.

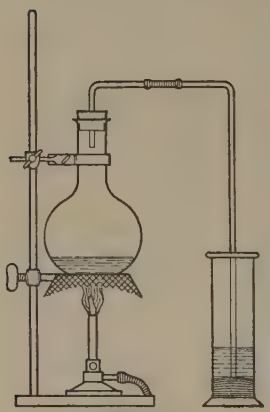


Fig. 91.

Silicon fluoride is a colourless gas which fumes in moist air, and has an irritant effect on the mucous membrane, even more pronounced than that of hydrochloric acid. As is evident from the previous experiment, it is decomposed by water.

477. Silicon Chloride, $SiCl_4$.—This is a fuming colourless liquid obtained either like the fluoride, by the direct union of silicon and chlorine, or by heating an intimate mixture of silica and carbon in a current of chlorine—

$$SiO_2 + 2\,C + 2\,Cl_2 = SiCl_4 + 2\,CO.$$

With water it forms gelatinous silica and hydrochloric acid—

$$SiCl_4 + 4\,H_2O = H_4SiO_4 + 4\,HCl.$$

It boils at 58° C. and the solid melts at — 89° C.

478. Silico-Chloroform, $SiHCl_3$.—This is a colourless liquid obtained by heating silicon or metallic silicides in hydrogen chloride—

$$Si + 3\,HCl = SiHCl_3 + H_2.$$

It is hydrolysed by water and is thus different from its analogue chloroform, $CHCl_3$. It boils at 33° C. and freezes at — 134° C.

Silico-fluoroform, $SiHF_3$, is also known.

Silicon Dioxide (*Silica*), SiO_2.

479. Occurrence and Preparation.—This is the only known oxide of silicon. It occurs *crystalline* as quartz and tridymite, and *amorphous* as opal, flint, and agate. It may also be prepared from certain mineral silicates, or silicates of the alkalies, by treating them with hydrochloric acid. It separates at first in the gelatinous form containing water, and if this gelatinous silica be heated the water is expelled, and anhydrous silica remains.

In the anhydrous condition, or in the mineral form, silica is unattacked by acids, with the exception of hydrofluoric acid; it can, however, be brought into solution again by fusion with alkaline carbonates.

Exp. 129. Mix thoroughly together silica and about four times its weight of fusion mixture, and heat in a porcelain crucible over the flame of a Bunsen burner. Presently the mass swells up and evolves large quantities of carbon dioxide—

$$\begin{matrix} Na_2CO_3 \\ K_2CO_3 \end{matrix} + 2\,SiO_2 = \underset{\text{(Sodium and potassium silicates)}}{\begin{matrix} Na_2SiO_3 \\ K_2SiO_3 \end{matrix}} + 2\,CO_2$$

After heating for half-an-hour, allow to cool, and extract with water, filtering off any insoluble matter (unattacked silica) which remains. The solution contains potassium silicate, together with potassium carbonate, which has been used in excess. Add strong hydrochloric acid to the solution until a marked acid reaction is obtained. If the solution is sufficiently concentrated, a flocculent precipitate of silica will be obtained. If, however, the solution be dilute, no immediate precipitate is obtained, though one may separate on standing or by boiling.

From such a solution a *soluble* form of silica may be prepared, as described in the next experiment (Exp. 130). It is probable that the solution contains the compound H_4SiO_4 called *orthosilicic acid*, but this acid has never been isolated. If the solution is left to evaporate *in vacuo* a translucent mass is left having the composition H_2SiO_3 and termed *metasilicic acid*. It is tasteless and possesses only a very feeble acid reaction.

Exp. 130. The solution from Exp. 129 contains potassium chloride, free hydrochloric acid, and silica. Make a shallow dish by binding parchment paper over a hoop of tin or gutta-percha, float this on a considerable body of water (Fig. 92), and pour the liquid into it. The potassium chloride and hydrochloric acid will slowly pass through the membrane and diffuse into the water, while the silica will remain behind in solution in the dish.

Sugar, salt, and such bodies behave like potassium chloride, and readily pass through such a membrane, whilst white of egg, caramel, and the like only do so extremely slowly. The former, from the fact that they are mostly crystallisable bodies, have been termed *crystalloids*, and the latter, from their gelatinous and amorphous nature, *colloids*. Silica is a colloid, and by means of this experiment it may be separated from such substances as common salt and potassium chloride, and obtained in solution. Under these circumstances we obtain silica in a form in which it is soluble in water.

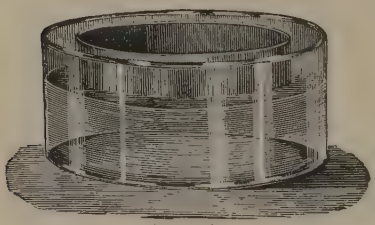


Fig. 92.

There is, however, a third modification intermediate between the soluble and insoluble forms, for when silica is freshly precipitated *in the cold*, it may be redissolved by the addition of dilute hydrochloric acid.

On standing, and more rapidly when boiled, this form becomes much less soluble, and ultimately passes in to the insoluble variety.

To sum up we have—

(1) Mineral silica (crystalline or amorphous) and anhydrous silica insoluble in and unattacked by the ordinary acids, with the exception of hydrofluoric acid.

(2) Gelatinous silica, soluble in dilute acids.

(3) Dialysed silica, soluble in water.

480. Silicon Carbide or Carborundum.—Silicon carbide or carborundum, SiC, is made commercially by heating a mixture of sand with excess of finely-ground anthracite or coke in the electric furnace—

$$SiO_2 + 3\,C = SiC + 2\,CO.$$

The furnace is arranged with permanent ends and temporary sides. A core of graphite is packed round with a finely-ground mixture of sand and anthracite or coke, to which has been added some salt to make the mass fusible and some sawdust to render it porous, and thus enable the carbon monoxide to escape. The electrodes are large carbon rods which project through the ends of the furnace into the mass. A strong electric current is passed, and after about 36 hours a zone of carborundum is obtained around the central core. The temporary sides are removed and the carborundum mass is broken up, treated with sulphuric acid, washed, dried, and graded.

Carborundum is a very hard crystalline substance. It is used extensively as an abrasive powder, for grinding-stones and wheels, and as a refractory material. It is not attacked by acids, and even resists the action of hydrofluoric acid. Its density is 3·2.

481. The Silicates.—These salts are chiefly interesting from the fact that they are largely represented in the mineral kingdom; the following list indicates some of those of more common occurrence :—

(1) Silicates of magnesium—

Olivine, Mg_2SiO_4, or $2\,MgO{\cdot}SiO_2$.

Talc, $Mg_3H_2Si_4O_{12}$, or $3\,MgO{\cdot}H_2O{\cdot}4\,SiO_2$.

Serpentine, $Mg_3Si_2O_7$, or $3\,MgO{\cdot}2\,SiO_2$.

(2) The Felspars—

Orthoclase, $KAlSi_3O_8$, or $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$ $(= 2\,KAlSi_3O_8)$.

Albite, $NaAlSi_3O_8$, or $Na_2O \cdot Al_2O_3 \cdot 6\,SiO_2$ $(= 2\,NaAlSi_3O_8)$.

Anorthite, $CaAl_2Si_2O_8$, or $CaO \cdot Al_2O_3 \cdot 2\,SiO_2$.

And the decomposition product of the felspars—

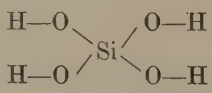
Kaolin, $H_4Al_2Si_2O_9$, or $2\,H_2O \cdot Al_2O_3 \cdot 2\,SiO_2$.

A glance at this list is sufficient to show that the composition of the silicates is often very complex. With the exception of those of the alkalies they are all practically insoluble in water, and for the most part they can only be brought into solution either by treatment with hydrofluoric acid or by fusion with alkaline carbonates.

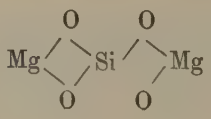
Aluminium silicate, $Al_2Si_2O_7 \cdot 2\,H_2O$, referred to above, is important as the main constituent of clay.

Sodium metasilicate, Na_2SiO_3, is prepared by treating silica with caustic soda. It is used extensively as "water glass" for preserving eggs.

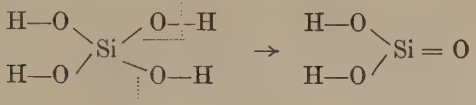
482. Constitution of the Silicic Acids and the Silicates.—The constitutional formula of orthosilicic acid, assuming that silicon is tetravalent, is—



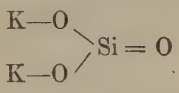
Olivine is the magnesium salt of this acid, and it has the formula—



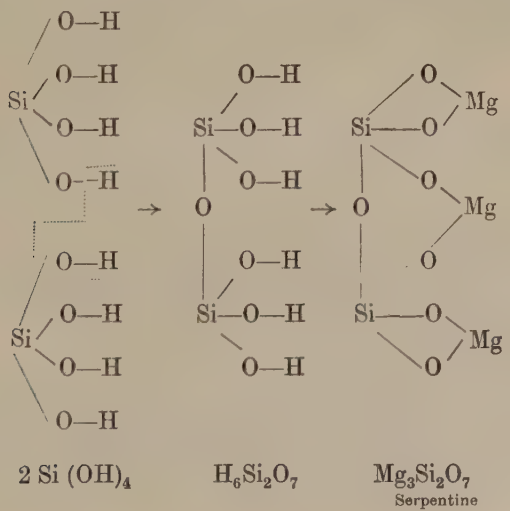
By the loss of one molecule of water from one molecule of orthosilicic acid metasilicic acid is obtained—



Potassium silicate is an example of a metasilicate; its constitutional formula is—

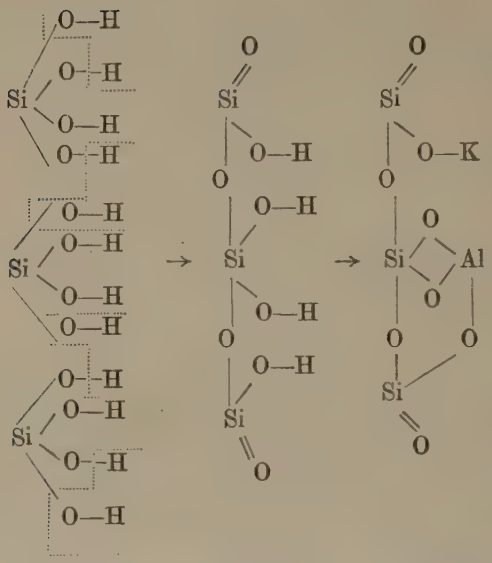


The more complex silicates are derived from acids which themselves may be derived from two or more molecules of orthosilicic acid by the elimination of one or more molecules of water. This will be made clear by the following examples:—



$2\,Si(OH)_4$ $H_6Si_2O_7$ $Mg_3Si_2O_7$

Serpentine



It will be noticed that in these complex silicates the atoms of silicon are not directly connected together as they are in complex carbon compounds, but are joined up through oxygen.

483. Detection and Estimation of Silicon. — Silicon is generally detected by fusion with fusion mixture, extraction with water, filtering, and then precipitating the silica with hydrochloric acid (Ex p. 129).

By this process followed by ignition, silica may be estimated. Silica may also be estimated by volatilising it as silicon fluoride by the action of hydrofluoric acid (§ 177), and thus finding the loss in weight, or by heating with calcium fluoride and concentrated sulphuric acid, and passing the silicon fluoride evolved into water (§ 476).

Boron.

484. History.—Borax, the chief natural compound of boron, has been known for many centuries, and was used by the Arabian chemists as a flux (*i.e.* buraq or borax).

Homberg, in 1702, obtained a white substance by adding sulphuric acid to a strong solution of borax (boric acid) which was subsequently called *sal sedativum*, but nothing was known then or for long afterwards about the chemical composition of these compounds.

Baron, in 1774, found that borax was a compound of *sal sedativum* and soda, and he suggested that sal sedativum was an acid, and gave to it the name "boracic acid," which was later abbreviated to "boric acid."

The element boron was obtained, about 1808, by Davy, and independently by Gay-Lussac and Thénard. The reduction of boron trioxide with potassium was the method employed.

485. Occurrence.—Boron is not found free in nature; its chief naturally-occurring compounds are *boric acid*, H_3BO_3, *tincal* or native borax, $Na_2B_4O_7.10\ H_2O$, *borocalcite*, $CaB_4O_7.4\ H_2O$, and *boracite*, $2\ Mg_3B_8O_{15}.MgCl_2$.

486. Preparation.—Boron is prepared by reducing its oxide, B_2O_3, by means of sodium, potassium, or magnesium in an atmosphere of hydrogen—

$$B_2O_3 + 6\ Na = 3\ Na_2O + 2\ B.$$

It is also obtained by the action of metallic potassium on boron trifluoride, BF_3, or on potassium fluoborate, KBF_4 (heat being required in the latter case)—

$$3\ K + BF_3 = B + 3\ KF.$$

$$3\ K + KBF_4 = B + 4\ KF.$$

In each of the above methods the reaction products are treated with hydrochloric acid, and the boron obtained as a brown powder, which is not very pure. Heating in an electric furnace in a vacuum at 1,200° C. serves to volatilise the impurities.

Pure boron can be made by passing an electric arc between copper electrodes in an atmosphere of boron trichloride vapour and excess of hydrogen—

$$2\,BCl_3 + 3\,H_2 = 2\,B + 6\,HCl.$$

487. Properties.—Prepared by these methods boron is an amorphous brown powder of density 2·34, which is very difficult to fuse and not readily oxidised: on strongly heating in air, however, it burns, forming boron trioxide, B_2O_3, and boron nitride, BN.

Nitric acid and hot strong sulphuric acid both oxidise boron, the latter converting it into boron trioxide and the former into the corresponding acid, H_3BO_3—

$$B + 3\,HNO_3 = H_3BO_3 + 3\,NO_2$$

$$2\,B + 3\,H_2SO_4 = B_2O_3 + 3\,H_2O + 3\,SO_2.$$

The water produced in the latter reaction is taken up by the excess of sulphuric acid.

On fusion with the hydroxides or various salts of the alkali metals boron is also oxidised to boron oxide, which combines with the hydroxide to form a borate—

$$2\,B + 6\,KOH = 2\,K_3BO_3 + 3\,H_2.$$

Unlike other non-metals, it is a conductor of electricity, its resistance being very small at a red heat.

When mixed with aluminium exposed to a white heat, and allowed to cool, the *crystalline* form of boron is obtained, the aluminium being removed by treatment with caustic soda. Prepared in this way it is, however, always associated with small quantities of carbon and aluminium.

Boron combines with many metals to form borides, which resemble the corresponding silicides (§ 474).

488. Boron Hydrides.—When magnesium boride, Mg_3B_2, obtained by heating together magnesium and boric acid, is treated with hydrochloric acid a mixture of various boron hydrides is obtained. By passing the mixture through a vessel surrounded with liquid air a white crystalline solid separates out, which according to Stock, consists of a number

of boron hydrides. The simple hydride, BH_3, is not known, but boroethane, B_2H_6, borobutane, B_4H_{10}, and others have been obtained.

Boroethane, B_2H_6 is a fairly stable gas; borobutane, B_4H_{10} is a liquid which boils at 16-17° C. and is spontaneously inflammable in air, burning with a green flame.

These two hydrides are decomposed by water as follows :—

$$B_2H_6 + 6\ H_2O = 2\ H_3BO_3 + 6\ H_2$$

$$B_4H_{10} + 12\ H_2O = 4\ H_3BO_3 + 11\ H_2.$$

489. Boron Trichloride, BCl_3.—Amorphous boron combines directly with chlorine without the application of heat. The trichloride may also be prepared by a method similar to that used for silicon tetrachloride, viz. by passing chlorine over an intimate mixture of the trioxide with carbon at a high temperature—

$$B_2O_3 + 3\ C + 3\ Cl_2 = 2\ BCl_3 + 3\ CO.$$

It is a colourless liquid boiling at 18° C. which fumes in air, and is readily decomposed by water, forming boric acid and hydrochloric acid—

$$BCl_3 + 3\ H_2O = H_3BO_3 + 3\ HCl.$$

In the anhydrous condition it is, however, very stable, and may even be distilled in contact with sodium without decomposition.

Fluorine combines energetically at ordinary temperatures with boron forming the trifluoride, BF_3, which may also be prepared by heating a mixture of boron oxide and fluorspar with sulphuric acid—

$$B_2O_3 + 3\ CaF_2 + 3\ H_2SO_4 = 2\ BF_3 + 3\ CaSO_4 + 3\ H_2O.$$

Bromine can also be made to combine directly with boron forming the tribromide, BBr_3.

490. Boron Nitride, BN.—Boron is one of the few elements which readily combine with nitrogen. The nitride is produced when boron is strongly heated in nitrogen, but is best prepared

by heating anhydrous borax, $Na_2B_4O_7$, with ammonium chloride—

$$Na_2B_4O_7 + 2\,NH_4Cl = B_2O_3 + 2\,BN + 2\,NaCl + 4\,H_2O.$$

The products, B_2O_3 and NaCl, may be removed by solution in water.

Boron nitride is a white amorphous powder, insoluble in water; it is decomposed on heating in steam with formation of ammonia and boron trioxide—

$$2\,BN + 3\,H_2O = B_2O_3 + 2\,NH_3.$$

491. Boron Oxide or Boric Anhydride, B_2O_3.—This and the boric acid and borates derived from it are the most important of the boron compounds. The oxide is formed when boron is burnt in air, but is usually prepared by heating boric acid to a high temperature—

$$2\,H_3BO_3 = B_2O_3 + 3\,H_2O.$$

Water is driven off and there remains a glassy-looking mass which when powdered combines slowly with water, forming boric acid (H_3BO_3) again.

492. Boric Acid, Orthoboric Acid, or Boracic Acid, H_3BO_3.—The jets of steam, or *suffioni*, issuing from cracks in the ground in the volcanic regions of Tuscany contain a small quantity of boric acid. The dilute solution obtained by the condensation of the steam is concentrated in pans which are heated by some of the jets of steam. On cooling, impure boric acid crystallises out. Boric acid is also manufactured from tincal, which is decomposed by hot concentrated hydrochloric acid—

$$Na_2B_4O_7 + 2\,HCl + 5\,H_2O = 4\,H_3BO_3 + 2\,NaCl.$$

On cooling, the acid separates out in thin laminae.

Exp. 131. Add concentrated hydrochloric acid to a hot strong solution of borax ($Na_2B_4O_7.10\,H_2O$). Allow to cool; filter off the crystals of boric acid which separate out and wash them with a little cold water. Note the soapy feel of the crystals.

493. Properties.—Boric acid is a crystalline solid slightly soluble in water and volatile in steam. It is a very weak acid which, like carbonic acid, gives with litmus a wine-red colour quite distinct from the bright red resulting from such acids as hydrochloric and sulphuric. It is a tri-basic acid, for the hydrogen of $B(OH)_3$ has been successively replaced by organic radicals. Boric acid dissolves in alcohol and, on igniting, the alcohol burns with a green flame, due to the volatilisation of some of the acid. Its solution colours turmeric paper brown, and on drying and adding alkali the stain turns black.

On heating to 100° C. boric acid loses water and is converted into *metaboric acid*, HBO_2, and on further heating to 140° C. more water is lost and pyroboric acid, $H_2B_4O_7$, is formed—

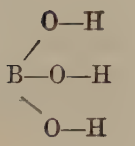
$$2\,H_3BO_3 = 2\,HBO_2 + 2\,H_2O.$$

$$4\,HBO_2 = H_2B_4O_7 + H_2O.$$

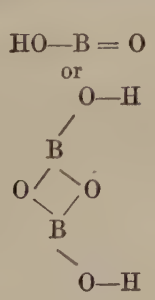
At a still higher temperature the remaining water is driven off, leaving boron trioxide or boric anhydride—

$$H_2B_4O_7 = 2\,B_2O_3 + H_2O.$$

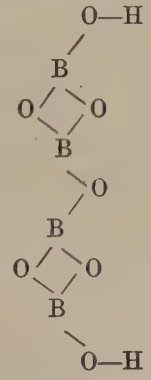
The following constitutional formulae illustrate the relation of the acids to each other—



Orthoboric acid.



Metaboric acid.



Pyroboric acid.

494. The Borates.—The salts derived from orthoboric acid are unstable, magnesium orthoborate, $Mg_3(BO_3)_2$, being one of the best known.

Metaboric acid, as represented in the lower formula given above, is a dibasic acid because its molecule contains two hydroxyl groups; this is in agreement with the fact that both normal and acid salts are known, *e.g.*—

Normal potassium metaborate	...	...	KBO_2
Acid potassium metaborate...	...	...	$KBO_2 \cdot HBO_2$ or KHB_2O_4.

A third class of salts is also known, called *superacid* salts; these are produced by the combination of a molecule of an acid salt with a molecule of the acid, *e.g.*—

Superacid potassium metaborate ... ... $KBO_2 \cdot 2\,HBO_2$.

Pyroboric acid is also dibasic; its best known salt is sodium pyroborate or borax, $Na_2B_4O_7 . 10\,H_2O$. (See *Inorganic Chemistry, Mainly Metals.*) Both the meta- and pyro-borates are much more stable than the orthoborates.

495. Perborates.—These can be prepared by the action of hydrogen peroxide on a borate or by the electrolytic oxidation of the borates of the alkalies. Sodium perborate, $NaBO_3 \cdot 4\,H_2O$ is used for bleaching in laundries, and is described in *Inorganic Chemistry, Mainly Metals.*

496. Detection and Estimation of Boron.—The borates (ortho-, meta- or pyro-), with the exception of those of the alkali metals, are only slightly soluble in water. When mixed with concentrated sulphuric acid and gently heated at the border of the Bunsen flame they impart a green colour to it, owing to the volatilisation of free boric acid. A similar coloration is also obtained when alcohol is added to such a mixture and ignited.

On liberating free boric acid from a borate by the addition of dilute hydrochloric acid, it behaves towards turmeric as already described, *i.e.* produces a brown coloration which is turned black by caustic soda.

When borax is fused on a platinum wire along with small quantities of compounds of chromium, cobalt, copper, manganese, or other metals, characteristic colours are imparted to it.

Boric acid has no action on methyl orange. It can be titrated with caustic soda if excess of glycerol or mannitol (with which it combines to form a fairly strong acid) is added to the solution, and phenolphthaleïn used as an indicator.

QUESTIONS.—CHAPTER XXV.

1. Mention any natural forms of silica either in the free state or in combination.

2. How are amorphous and crystalline silicon respectively prepared? With what elements does silicon combine directly?

3. Express by equations the action of (1) hydrofluoric acid, (2) caustic potash on silicon.

4. Compare the properties of amorphous and crystalline silicon.

5. How is silicon hydride prepared, and what is the effect of heating it (*a*) in absence of air, (*b*) in presence of air?

6. Describe two methods by which silicon fluoride may be obtained. How does this compound react with water?

7. How are silicon chloride and silicon chloroform obtained? What is the action of water on these two substances?

8. Under what circumstances is gelatinous silica obtained, and how may it be converted into the anhydrous form of silica?

9. How may a solution of silica be prepared and separated from any sodium chloride which may be associated with it?

10. Give a general description of the silicates, pointing out any characteristic properties which they possess.

11. State what you know of the history of silicon and boron.

12. Give two methods by which boron may be prepared. What is the action of the following substances on boron: (1) nitric acid, (2) sulphuric acid, (3) caustic potash? State the conditions under which the action takes place in each case and give equations.

13. Say what you know of the hydrides of boron.

14. How is boron nitride prepared? Under what conditions does it decompose water, and what are the products?

15. Compare the allotropic forms of carbon, silicon, and boron.

16. In what minerals does boron occur, and how may boric acid be obtained from these minerals?

17. What is the action of heat on boric acid?

18. Give the constitutional formulae for the acids derived from the oxide B_2O_3.

19. Give the general characteristics of the borates, and show how you would detect the presence of a borate.

20. Compare and contrast carbon with silicon and boron.

APPENDIX I.

THE METRIC SYSTEM OF WEIGHTS AND MEASURES.

The metric system has been found the most convenient for operations in which weighing and measuring are concerned, and it is universally used in scientific work.

The *unit of length* in this system is the *metre*, which is equivalent to 39·37 in. One-hundredth of the metre is called a *centimetre*.

The *unit of volume* is the *cubic centimetre*, that is, it is the volume of a cube whose side is one centimetre. This unit volume is equivalent to nearly one-sixteenth of a cubic inch.

The *unit of weight* is the weight of this volume, *i.e.* one cubic centimetre, of water, the temperature being that at which water has its maximum density, viz. 4° C. This weight is termed the *gramme*, and is equivalent to 15·432 grains.

The prefix *kilo* indicates the multiple 1,000; thus 1 kilogramme = 1,000 grammes = 15,432 grains = about 2·2 lb.

The prefixes *deci*, *centi*, and *milli* respectively indicate the fractional parts $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$.

1 decimetre	=	$\frac{1}{10}$ metre	= 3·937	inches.
1 centimetre	=	$\frac{1}{100}$,,	= 0·3937	,,
1 millimetre	=	$\frac{1}{1000}$,,	= 0·03937	,,
1 decigramme	=	$\frac{1}{10}$ gramme	= 1·5432	grains.
1 centigramme	=	$\frac{1}{100}$,,	= 0·15432	,,
1 milligramme	=	$\frac{1}{1000}$,,	= 0·015432	,,

A measure of volume very frequently employed is the *litre*, which is the volume occupied by a kilogramme of water at 4° C.; it is therefore equivalent to a cubic decimetre, or 1,000 cubic centimetres or, in English measure, 61·027 cubic inches.

APPENDIX II.

TABLES FOR REDUCTION OF MOIST GAS TO STANDARD CONDITIONS.

The volume of a moist gas having been measured at a given temperature and pressure, it is necessary to first find what volume the *dry* gas would occupy at 0° C. and 760 mm. pressure. Allowance must be made for (see Chap. V.)—

(*a*) the temperature of the gas (*i.e.* of the room);

(*b*) the pressure to which it is subjected (that of the atmosphere at the time of the experiment);

(*c*) the tension, *i.e.* pressure, of the water-vapour present.

This involves a somewhat complex calculation, and a table has therefore been drawn up to enable the student to make the correction by using the factor given in the table.

Thus suppose the temperature of the laboratory to be 10° C. and the atmospheric pressure 740 mm.; the tension of aqueous vapour with which the gas is saturated is for 10° C., 9·1 mm. Now if v is the volume of the moist gas as observed, then V the volume of the dry gas at 0° C. and 760 mm. pressure is given by the expression—

$$V = \frac{v \times 273 \times (740 - 9{\cdot}1)}{283 \times 760} = 0{\cdot}928\ v.$$

To deduce the volume of the dry gas at standard temperature and pressure from the observed volume it is therefore only necessary to *multipy this latter by the factor* 0·928 as taken from the table, and so for any other temperature or pressure.

Pressure.	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
730 mm.	0·915	0·907	0·899	0·891	0·882	0·874
740 ,,	0·928	0·920	0·911	0·903	0·895	0·886
750 ,,	0·940	0·932	0·924	0·915	0·907	0·898
760 ,,	0·953	0·945	0·936	0·928	0·919	0·910
770 ,,	0·966	0·957	0·949	0·940	0·932	0·923

For intermediate temperatures or pressures, the value may be expressed with sufficient accuracy by taking the proportional mean; *e.g.* for 10° C. and 745 mm. we shall find 0·934, and for 11° C. and 750 mm. we shall find 0·936.

If we desire to know the *weight* of the hydrogen liberated, the following table may be used. Taking the weight of a litre of dry hydrogen under standard conditions as 0·09 gramme the table gives the weight of hydrogen in a litre of the moist gas collected at the temperature and pressure given.

Pressure.	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
730 mm.	0·0824	0·0816	0·0809	0·0802	0·0794	0·0787
740 ,,	0·0835	0·0828	0·0820	0·0813	0·0806	0·0798
750 ,,	0·0846	0·0839	0·0832	0·0824	0·0816	0·0808
760 ,,	0·0858	0·0851	0·0843	0·0835	0·0827	0·0820
770 ,,	0·0869	0·0861	0·0854	0·0846	0·0839	0·0831

An example will make the method of using the table quite clear—

Thermometer, 16° C. Barometer, 750 mm.

Observed volume of gas, 120 c.cm.

The factor under 16° C. and 750 mm. is 0·0824.

$$\therefore \text{ Weight of hydrogen} = \frac{0{\cdot}0824 \times 120}{1000} = 0{\cdot}00988 \text{ grm.}$$

APPENDIX III.

International Atomic Weights (0 = 16).

Element.	Symbol.	Atomic Weight.	Atomic No.	Element.	Symbol.	Atomic Weight.	Atomic No.
Aluminium ...	Al	26·97	13	Neodymium ...	Nd	144·3	60
Antimony	Sb	121·77	51	Neon	Ne	20·20	10
Argon	A	39·9	18	Nickel	Ni	58·68	28
Arsenic	As	74·96	33	Niobium (see Columbium)	Nb	93·1	41
Barium	Ba	127·37	56	Niton (radium emanation)	Nt	222 0	86
Beryllium (glucinum)	Be	9·1	4	Nitrogen	N	14·008	7
Bismuth	Bi	209·0	83	Osmium	Os	190 9	76
Boron	B	10·9	5	Oxygen	O	16·00	8
Bromine	Br	79·92	35	Palladium	Pd	106·7	46
Cadmium	Cd	112·40	48	Phosphorus ...	P	31·04	15
Caesium	Cs	132·81	55	Platinum	Pt	195·2	78
Calcium	Ca	40·07	20	Polonium	Po	210·0	84
Carbon	C	12·00	6	Potassium	K	39·10	19
Cerium	Ce	140 25	58	Praseodymium	Pr	140·9	59
Chlorine	Cl	35·46	17	Radium	Ra	226·0	88
Chromium ...	Cr	52·0	24	Rhodium	Rh	102·9	45
Cobalt	Co	58·97	27	Rubidium	Rb	85·45	37
Columbium (niobium) ...	Cb	93·1	41	Ruthenium ...	Ru	101·7	44
Copper	Cu	63·57	29	Samarium	Sa	150·4	62
Dysprosium ...	Dy	162 5	66	Scandium	Sc	45·1	21
Erbium	Er	167·7	68	Selenium	Se	79 2	34
Europium	Eu	152·0	63	Silicon	Si	28·3	14
Fluorine	F	19·00	9	Silver	Ag	107·88	47
Gadolinium ..	Gd	157·3	64	Sodium	Na	23 00	11
Gallium	Ga	70·10	31	Strontium	Sr	87·63	38
Germanium ...	Ge	72·5	32	Sulphur	S	32·06	16
Gold	Au	197·2	79	Tantalum	Ta	181·5	73
Helium	He	4·00	2	Tellurium	Te	127·5	52
Holmium	Ho	163·5	67	Terbium	Tb	159·2	65
Hafnium	Hf	178·6	72	Thallium	Tl	204·0	81
Hydrogen	H	1·008	1	Thorium	Th	232·15	90
Indium	In	114·8	49	Thulium	Tm	168·5	60
Iodine	I	126·92	53	Tin	Sn	118·7	50
Iridium	Ir	193·1	77	Titanium	Ti	48·1	22
Iron	Fe	55·84	26	Tungsten	W	184·0	74
Krypton	Kr	82·92	36	Uranium	U	238·2	92
Lanthanum ...	La	139·0	57	Vanadium	V	51·0	23
Lead	Pb	207·20	82	Xenon	Xe	130·2	54
Lithium	Li	6·94	3	Ytterbium (Neoytterbium)	Yb	173·5	70
Lutecium	Lu	175·0	71	Yttrium	Yt	89·33	39
Magnesium ...	Mg	24·32	12	Zinc	Zn	65·37	30
Manganese ...	Mn	54·93	25	Zirconium	Zr	90·6	40
Mercury	Hg	200·6	80				
Molybdenum	Mo	96·0	42				

ANSWERS.

(*a*) ANSWERS TO CHEMICAL CALCULATIONS IN CHAPTER X.

1. 91°.
2. 293 : 253.
3. 50 c.cm., 90·9 c.cm., 140·9 c.cm.
4. 2090 c.cm., 418 c.cm., 104·5 c.cm., 38 c.cm.
5. 441 c.cm.
6. 129·7 c.cm.
7. 488 mm.
8. 273° C.
9. 3,947 atmospheres.
10. 6,888 atmospheres.
11. 571·4 c.cm.
12. 152·2 grm.; 65·7 c.cm.
13. 73·9 c.cm.; 180·4 grm.
14. Ca = 40 per cent.
    C = 12 ,,
    O = 48 ,,
    44 per cent.
15. H = 7·44 per cent.
    Cl = 33·02 ,,
    O = 59·54 ,,
16. FeS_2.
17. Fe_3O_4.
18. $Na_6P_4O_{13}$.
19. 465·7 grm.
20. 81·8 c.cm.
21. 4·852 grm.
22. 17·91 litres.
23. 2·446 grm.
24. 72 litres; 142·6 grm.
25. Oxygen, 23; Oxygen, 20·7.
    Nitrogen, 77; Nitrogen, 79·3.
26. Hydrogen, 11·1.
    Oxygen, 88·9.
27. 4·622 litres.
28. (*a*) N = 7·5 c.cm.
    H = 22·5 c.cm.
    O = 40·0 c.cm.
    (*b*) N = 7·5 c.cm.
    O = 28·75 c.cm.
29. Oxygen = 3·73 c.cm.
    Carbon dioxide = 16·36 c.cm.
30. Oxygen = 0·37 c.cm.
    Carbon dioxide = 163·6 c.cm.
31. 3·534 per cent.
32. 61023; 28·317.
33. 42·1 per cent.
    0·157 litre.
34. 180 c.cm.; 140 c.cm.
35. 14·18 grm.
36. 100 c.cm.; 0·072 grm.
37. 29 per cent.
38. 252·0 kilog.
39. Nitrogen, 79·00 per cent.
    Oxygen, 18·88 ,,
    Carbon dioxide, 2·12 ,,

(*b*) ANSWERS TO QUESTIONS.

CHAP. XI. (18) 0·001429 grm. per c.cm.

CHAP. XIII. (5) 11·205 grm. of hydrogen; 88·795 grm. of oxygen.

CHAP. XVII. (6) 19·6. (7) 78·49, 0·68, 20·83. (8) 22·97.

CHAP. XXI. (25) Disodium hydrogen phosphate, Na_2HPO_4; 88·75 grm.

CHAP. XXII. (3) 4399 tons. (23) 0·57 per cent. (24) 1146·7 c.cm. (25) 30 c.cm.; 20 c.cm. (26) 60 c.cm. of oxygen. (27) 85 c.cm.; 55 c.cm. of oxygen, 20 c.cm. of carbon dioxide, 10 c.cm. of water vapour.

CHAP. XXIII. (13) 8550 c.cm., 2020 c.cm.

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